

CHAPTER III

IMPORTANT THERMODYNAMIC FUNCTIONS FROM EQUATION OF STATE

3.1 Used In Process Calculations.

In chemical engineering calculation, we often need to know the values of some thermodynamic properties of the system (fluid, solution, mixture). Among the properties that appear frequently are $P, V, T, H, U, f, \phi, \gamma_i, c_p,$ and c_v . These thermodynamic properties can be calculated from equations of state by using equations that relate the thermodynamic properties. In the process calculations, the important thermodynamic properties are enthalpy, entropy, fugacity coefficient functions, vapor pressure, and liquid and vapor compressibility factors.

3.2 Formula In Terms Of P-V-T.

Edmister and Lee (1984)[1], The basic information needed in applying thermodynamics to the solution of scientific and engineering problems are pressure, volume, temperature, and composition for the fluids of interest. Because of its practical and theoretical importance, a large amount of P-V-T and mixture data have been measured and accumulated for most of the essential fluids such as air, water (steam), many hydrocarbons, and other chemicals. Though not essential for hydrocarbon systems, the P-V-T data of monoatomic gases, such as argon, have also

been extensively measured with high precision to study the effect of molecular dynamics and interactions on the volumetric behavior or vice versa. The measurements are expected to provide more knowledge and deeper understanding of the P-V-T behavior of many different kind of fluids.

3.2.1 Thermodynamic Functions.

Internal energy:

$$\Delta U = Q + W \quad (3-1)$$

Enthalpy:

$$H = U + PV \quad (3-2)$$

Helmholtz free energy:

$$A = U - TS \quad (3-3)$$

Gibbs free energy:

$$G = H - TS. \quad (3-4)$$

Because thermodynamics is only capable of describing the changes of system properties, it is more convenient to express the four defined functions in differential forms.

$$dU = TdS - PdV. \quad (3-5)$$

Differentiating Equations (3-2) and (3-3), and combining with Equation (3-5) gives

$$dH = TdS + VdP, \quad (3-6)$$

$$dA = -SdT - PdV. \quad (3-7)$$

Differentiating Equation (3-4) and combining with Equation (3-6) gives

$$dG = -SdT + VdP \quad (3-8)$$

3.2.2 Properties as Functions of T and V .

Now the change in U, H, A , or G between any two states can, in principle, be calculated by integrating the appropriate differential Equation, (3-5), (3-6), (3-7), or (3-8). Derivations of equations for thermodynamic functions as functions of T and V are presented here.

3.2.2.1 Enthalpy, $H(T, V)$.

$$\left\{ dH = d(PV) + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \right\}_T \quad (3-9)$$

Integrating Equation (3-9) at constant T from zero pressure condition to actual condition, and recognizing that $\lim_{P \rightarrow 0} Z = 1$ and $PV = RT$, at $P = 0$, results in Equation (3-10).

$$\frac{H - H^*}{RT} = Z - 1 + \frac{1}{RT} \int_{\infty}^V \left[T \left(\frac{\partial V}{\partial T} \right)_v - P \right] dV \quad (3-10)$$

Equations of state provide the P-V-T relation required to evaluate the right side of the above equation. The values of the ideal gas state enthalpy, H^* , in the left side of Equation (3-10) are given for pure substances, and can be calculated for equation:

$$H^* = \sum_i^N x_i H_i^* \text{ for mixtures.} \quad (3-11)$$

3.2.2.2 Entropy, $S(T, V)$.

The entropy expression may be derived in a similar manner to the enthalpy, except that the ideal gas state expression requires a special mathematical manipulation. The isothermal form is more practical for the integration of Equation (3-12) from (T, P^*) to (T, P) along real path gives Equation (3-13).

$$dS = \left(\frac{\partial P}{\partial T} \right)_v dV \Bigg|_T \quad (3-12)$$

$$\frac{S - S_0^*}{R} + \ln \frac{P}{P_0} = \ln Z + \frac{1}{R} \int_{\infty}^V \left[\left(\frac{\partial P}{\partial T} \right)_v - \frac{R}{V} \right] dV \quad (3-13)$$

Now, (T, P^*) can be safely replaced by ∞ , as the integrands no longer are infinite at $P = 0$ (or at $V = \infty$). For mixtures, it gives

$$S_0^* = \sum_i^N x_i (S_{0i}^* - R \ln x_i) \quad (3-14)$$

3.2.2.3 Fugacity Coefficient, $f / P(T, V)$ (ϕ).

$$d \ln \frac{f}{P} + d \ln(PV) = d \left(\frac{PV}{RT} \right) + \left(\frac{1}{V} - \frac{P}{RT} \right) dV \quad (3-15)$$

Integrating the above equation and also noting that $PV = RT$ and $\phi = \infty$ at $P = 0$ results in

$$\ln \frac{f}{P} = Z - 1 - \ln Z + \frac{1}{RT} \int_{\infty}^V \left(\frac{RT}{V} - P \right) dV \quad (3-16)$$

3.2.2.4 Vapor Pressure.

For a system containing N components and M phases, it provides an alternative phase equilibrium criterion as follows:

$$\hat{f}_i^{(1)} = \hat{f}_i^{(2)} = \dots = \hat{f}_i^{(M)} \quad (i = 1, 2, \dots, N) \quad (3-17)$$

The fugacity of each component in a mixture is identical in all phases at equilibrium. This is equally true for a single component system having vapor and liquid phases at equilibrium. In this case, Equation (3-17) reduces to,

$$f_i^V = f_i^L \quad (3-18)$$

where f_i^V and f_i^L are the pure component fugacities of vapor and liquid respectively. This equation is valid at any point on the saturation curve, where the vapor and liquid coexist in equilibrium.

The pure component fugacity expression is derived from Equation (3-16) in the fugacity coefficient form. Writing Equation (3-16) for both vapor and liquid, subtracting the two expressions and combining with Equation (3-18) gives

$$\ln\left(\frac{f^V}{f^L}\right) = 0 \quad (3-19)$$

Equation (3-19) is valid for pure fluids along the saturation curve where the vapor and liquid phases coexist in equilibrium. And at this condition, the pressure is the saturated vapor pressure.