8.8 CALCULATION OF FUGACITY (LIQUIDS)

Example S8.1 Vapor and Liquid Fugacities using the Virial Equation

Determine the fugacity (MPa) for acetylene at: (a) 250K and 10 bar; (b) 250K and 20 bar. Use the virial equation and the shortcut vapor pressure equation.

Solution:

From the back flap of the text for acetylene: T_c = 308.3 K, P_c = 6.139, ω = 0.187, Z_c = 0.271.

For each part of the problem, the fluid state of aggregation is determined before the method of solution is specified. At 250 K, using the shortcut vapor pressure equation, Eqn 8.11, the vapor pressure is P^{sat} = 1.387 MPa.

We anticipate the need to calculate the virial coefficient at 250K using Eqns. 6.8-6.9:

T_r = 250/308.3 = 0.810, B^o = – 0.5071, B^1 = – 0.2758, B = -233.3 cm^3/mol.

(a) P = 1 MPa < P^{sat} so the acetylene is vapor. Using Eqn 6.10 to evaluate the appropriateness of the virial equation at 1 MPa, P_r = 1/6.139 = 0.163, and 0.686 + 0.439P_r = 0.76 and T_r = 0.810, so the correlation should be accurate.

Using Eqn 8.29,

$$\ln\varphi = \frac{BP}{RT} = \frac{-233.3(1)}{8.314(250)} = -0.11224$$

$f = \varphi P$ = 0.894 (1) = 0.894 MPa

(b) P = 2 MPa > P^{sat} so the acetylene is liquid. For a liquid phase, the only way to incorporate the virial equation is to use the Poynting Method, Eqn 8.36. Using Eqn 6.10 to evaluate the appropriateness of the virial equation at the vapor pressure, P_r^{sat} = 1.387/6.139 = 0.2259, and 0.686 + 0.439P_r^{sat} = 0.785, and T_r = 0.810, so the correlation should be accurate.

At the vapor pressure,

$$\ln\varphi^{sat} = \frac{BP^{sat}}{RT} = \frac{-233.3(1.387)}{8.314(250)} = -0.156$$

$f^{sat} = \varphi^{sat} P^{sat}$ = 0.8558(1.387) = 1.187 MPa

Using the Poynting method to correct for pressure beyond the vapor pressure will require the liquid volume, estimated with the Rackett Eqn 8.37, using $V_c = Z_c RTc/P_c$ = 0.271(8.314)(308.3)/6.139 = 113.2 cm^3/mol.

$$V^{satL} = 113.2(0.271)^{(1-0.8109)^{0.2857}} = 50.3\ cm^3/mol$$

The Poynting correction is given by Eqn 8.35,

$$\frac{f}{f^{sat}} = \exp\left(\frac{50.3(2-1.387)}{8.314(250)}\right) = 1.015$$

Thus f = 1.187(1.015) = 1.20 MPa. The fugacity is close to the value of vapor pressure for liquid acetylene, even though the pressure is 2 MPa.