Thermodynamics II

Fugacity Calculation: Examples

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Example

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.

for acetylene: $T_c = 308.3$ K, $P_c = 6.139$, $\omega = 0.187$, $Z_c = 0.271$.

At 250 K, $P^{sat} = 1.387$ MPa.

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Example cont.

Example cont.

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Example

Determine the fugacity, in bars, for R134a for a Redlich-Kwong gas at 90 °C and 10 bar. Compare against Van der Waals EOS.

$$p = \frac{RT}{v-b} - \frac{a}{\sqrt{T}\, v\,(v+b)}, \qquad a = 0.42748\frac{R^2 T_c^{2.5}}{P_c}, \qquad b = 0.08664\frac{RT_c}{P_c}$$

In R134, $(C_2F_4H_2)$, we have $T_c = 374.3\ K$, $P_c = 40.6\ bar$, $M = 102.3\ kg/kmol$.

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Example cont.

$$RT\ln\frac{f}{f_0} = Pv - P_0 v_0 - \int_{v_0}^{v} P\,dv$$

$$\ln f = \frac{b}{v-b} + \ln\frac{RT}{v-b} - \frac{a}{RT^{3/2}}\left[\frac{1}{v+b} + \frac{1}{b}\ln\frac{(v+b)}{v}\right]$$

$$\ln\phi = \int_0^P \left(\frac{\bar{V}}{RT} - \frac{1}{P}\right)\partial P$$

$$\ln\phi = \ln\left(\frac{\bar{V}}{\bar{V}-b}\right) + \frac{b}{\bar{V}-b} - \frac{2a}{RT^{3/2}b}\ln\left(\frac{\bar{V}+b}{\bar{V}}\right) + \frac{a}{RT^{3/2}b}\left(\ln\left(\frac{\bar{V}+b}{\bar{V}}\right) - \frac{b}{\bar{V}+b}\right) - \ln\frac{P\bar{V}}{RT}$$

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Example cont.

; the specific volume directly from the EOS $\left(v = 2.724\ m^3/kg\right)$:

➡ $f = 9.09\ bar$

for a Van der Waals gas

$$P = \frac{RT}{(\bar{V}-b)} - \frac{a}{\bar{V}^2}$$

Where $a = \frac{27R^2T_c^2}{64P_c}$ $\quad b = \frac{RT_c}{8P_c}$

$$\ln f = \frac{b}{v-b} + \ln\frac{RT}{v-b} - \frac{2a}{RTv}$$

$$\ln\phi = \ln\left(\frac{\bar{V}}{\bar{V}-b}\right) + \frac{b}{\bar{V}-b} - \frac{2a}{\bar{V}RT} - \ln\frac{P\bar{V}}{RT}$$

$f = 9.21\ bar$.

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Example

For H_2O at a temperature of 573.15 K (300°C) and for pressures up to 10 000 kPa (100 bar) calculate values of f_i and ϕ_i from data in the steam tables and plot them vs. P.

Example cont.

Example cont.

Example

Estimate $\hat{\phi}_1$ and $\hat{\phi}_2$ by Eqs. (11.59) and (11.60) for an equimolar mixture of methyl ethyl ketone(1)/toluene(2) at 323.15 K (50°C) and 25 kPa. Set all $k_{ij} = 0$.

Example cont.

Example cont.

Example cont.

HW

Calculate the fugacity and fugacity coefficient for water for the temperature range 300 to 1000 ^{o}C and pressure 1000 to 10000 bar using

1. Steam table data
2. Van der Waals equation
3. Redlich-Kwong equation

Show that

$$RT \ln \frac{f_i}{y_i P} = RT \ln \hat{\phi}_i$$

$$= \int_{v=\infty}^{v} \left[-\left(\frac{\partial P}{\partial n_i} \right) + \frac{RT}{n_T v} \right] \cdot \partial(n_T v) - RT \ln z$$

HW

Show that

$$\ln\frac{f}{P} = \frac{-1}{RT}\int_{P=0}^{P}\left(\frac{RT}{P} - v\right)dP$$

$$= z - 1 - \ln z - \frac{1}{RT}\int_{v=\infty}^{v}\left(P - \frac{RT}{v}\right)dv$$

1. Volume-explicit EOSs, like the little EOS, are useful for vapors whose behavior is close to ideal gas behavior. They are not useful for gases far from the ideal gas state.
2. Pressure-explicit EOSs can represent both liquid and vapor and behavior near the critical state with fair accuracy for simple EOSs (like cubic EOSs) and very good accuracy for more complex EOSs, like the BWR EOS.
3. With suitable mixing rules, these pressure-explicit EOSs can make good-to-excellent estimates of high-pressure VLE. They are very widely used for that purpose.
4. This appendix has more mathematics than seems appropriate in the main text.