# CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)

## 03. FUGACITY IN PURE COMPONENT SYSTEMS

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# Outline

- Residual Gibbs Energy
- Definition of Fugacity
- Chemical equilibrium in Terms of Fugacity
- Fugacity in the Ideal-Gas State
- Relationship of Fugacity to the Gibbs Energy
- Why Use Fugacity?
- Roadmap to Fugacity
- Calculation of Fugacity for Compressed Liquids—Poynting Equation

# Residual Gibbs Energy

- Chemical equilibria establishes the equality of the molar Gibbs energy of the phases that are present.
- Alternative forms suitable for calculations can be obtained.
- First, express the Gibbs energy in terms of its residual:

$$G = G^{\mathrm{IG}} + G^{\mathrm{R}}$$

- This equation can be written for the any phase e.g., liquid and vapor.
  - The ideal-gas term is the same in both phases because it depends only on temperature and pressure, which are the same in both phases.
  - Conclusion: residual Gibbs energy of the phases are also equal:

$$G_L^{\mathrm{R}} = G_V^{\mathrm{R}}$$

# Definition of Fugacity

- The equality of residual Gibbs energies among phases is equivalent to the chemical equilibria equation, but has the advantage that it involves residual properties, whose calculation does not require a reference state.
- *Fugacity* is introduced using the following definition:

$$f = P \exp\left[\frac{G^{\mathrm{R}}}{RT}\right] = \phi P$$

  - Fugacity coefficient is defined as

$$\phi = \exp\left[\frac{G^{\mathrm{R}}}{RT}\right] \Rightarrow \ln\phi = \frac{G^{\mathrm{R}}}{RT}$$

produced by Dr. Lucas Landherr through a Provost Advancing Undergraduate Teaching and Learning Grant at Northeastern University

Northeastern

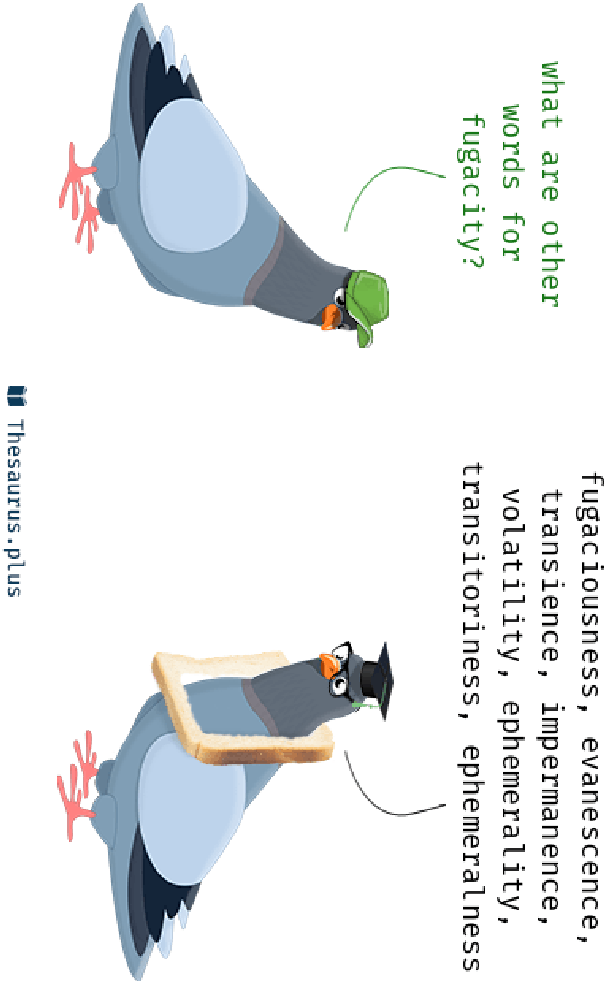
# Chemical equilibrium in Terms of Fugacity

- Since the residual Gibbs energy is the same in both phases, the fugacity at saturation satisfies the conditions:

$$f^{V} = f^{L}$$

$$\phi^{V} = \phi^{L}$$

- The equality of fugacities is an alternative statement of the necessary and sufficient condition for phase equilibrium
  - It is the basis for all phase equilibria calculations, whether we are dealing with pure substances or with mixtures.
  - The equality of the fugacity coefficients is a special result and applies to pure substances only.

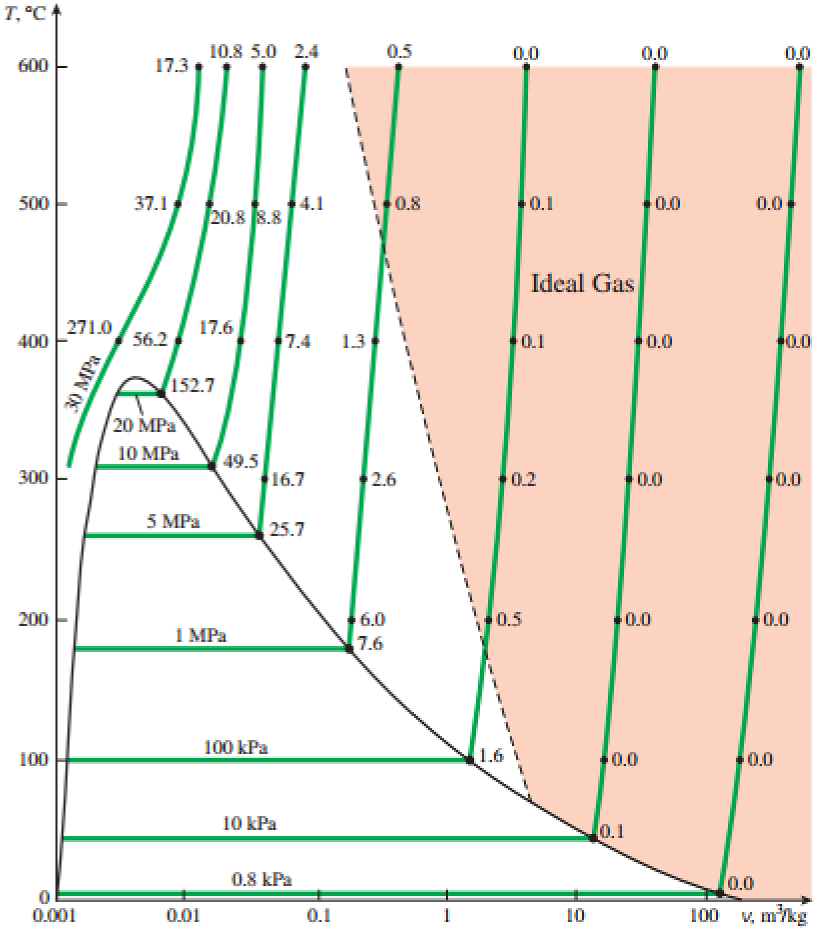


# Fugacity in the Ideal-Gas State

- The limiting values of fugacity and its coefficient in the ideal-gas limit follow easily by noting that $G^R = 0$ in this limit:

$$\lim_{P \to 0} f = f^{\mathrm{IG}} = P$$

$$\lim_{P \to 0} \phi = \phi^{\mathrm{IG}} = 1$$



# Relationship of Fugacity to the Gibbs Energy

- The term fugacity comes from the Latin *fugere* ("to flee")
  - Refers to the tendency of species to "escape" to the more stable phase.
- Fugacity is an auxiliary property related to the Gibbs energy which is a fundamental thermodynamic property at equilibrium.

$$G(T,P) = G_0(T,P_0 \to 0) + RT\ln\frac{f(T,P)}{f_0(T,P_0 \to 0)} = G_0 + RT\ln\frac{f}{f_0}$$

- At a constant T and from definition of G

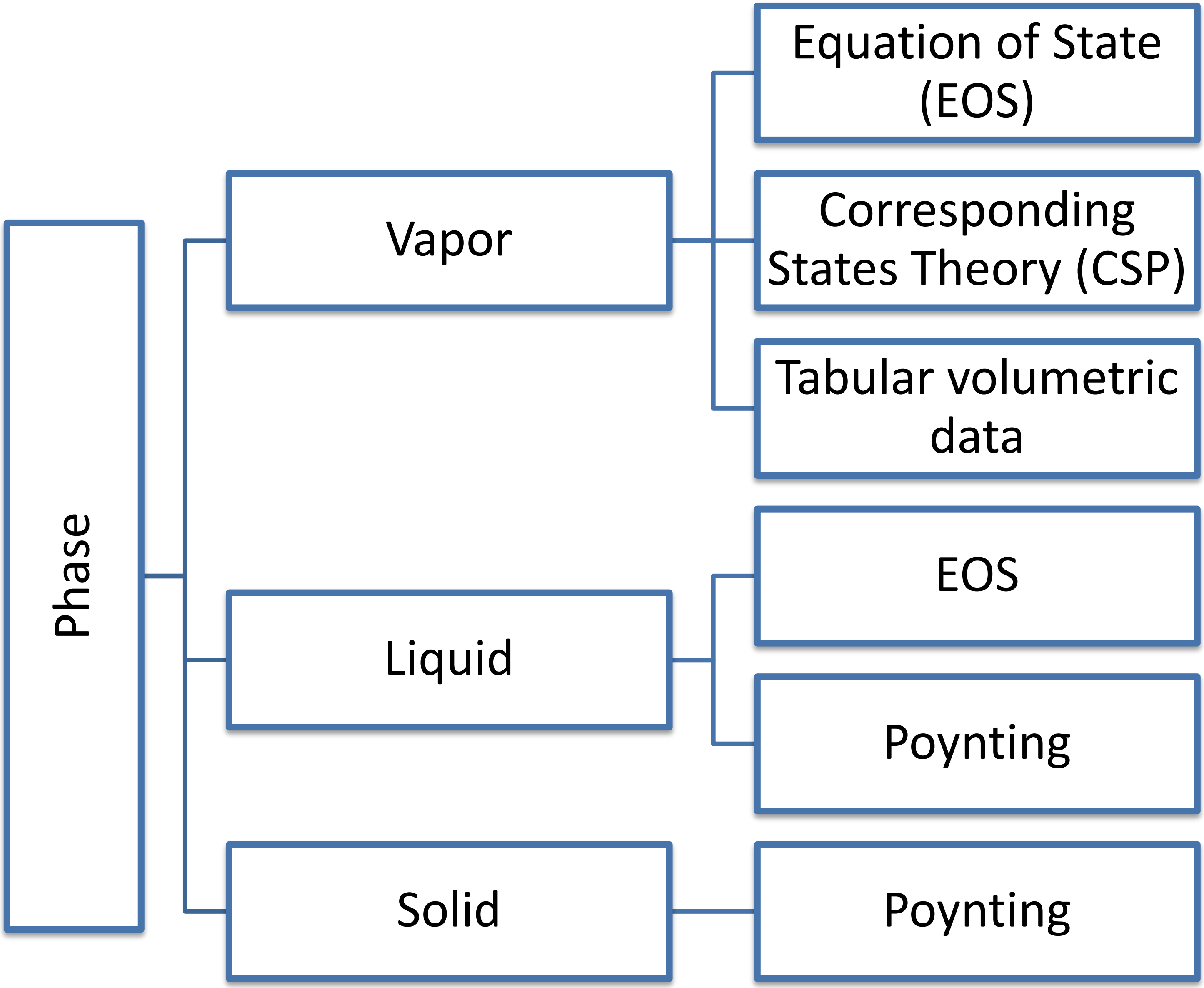
$$d\ln\frac{f}{f_0} = \frac{V}{RT}dP \quad \to \quad \ln\frac{f}{f_0} = \int_{P\to 0}^{P}\frac{V}{RT}dP$$

# Why Use Fugacity?

- Fugacity is equivalent to the Gibbs energy with respect to defining the conditions of phase equilibrium.

| Fugacity | Gibbs energy: |
|---|---|
| • Does *not* require a reference state. | • Requires a reference state. |
| • Has a well defined (and simple) value in the ideal-gas state. | • Its value in the ideal-gas state ($P \to 0$) approaches $-\infty$. |

# Roadmap to Fugacity



Phase

Vapor

Equation of State (EOS)

Corresponding States Theory (CSP)

Tabular volumetric data

Liquid

EOS

Poynting

Solid

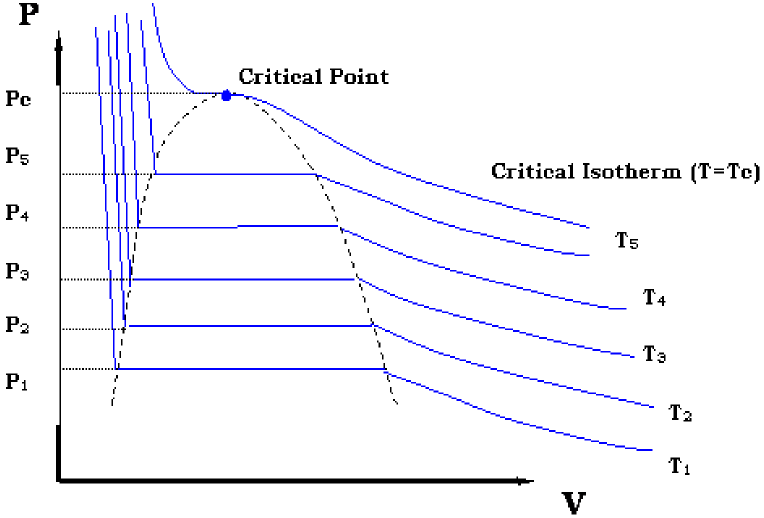
Poynting

# Calculation of Fugacity for Compressed Liquids—Poynting Equation

- Molar volume is essentially independent of pressure for compressed liquids:

$$\ln\frac{f}{f_0}=\int_{P\to 0}^{P}\frac{V}{RT}dP=\frac{(P-P_0)}{RT}V$$

Poynting factor



- A practical result is obtained if we choose the initial state to be the saturated liquid at the prescribed T:

$$f(T,P)=f_L(T,P^{\text{sat}})\exp\left[\frac{(P-P^{\text{sat}})}{RT}V_L\right]$$

$$=\phi^{\text{sat}}(T,P^{\text{sat}})P^{\text{sat}}(T)\exp\left[\frac{(P-P^{\text{sat}})}{RT}V_L\right]$$

# Example **7.4-Matsoukas**: Saturated Liquid

Calculate the fugacity and fugacity coefficient of saturated liquid water at 25°C.

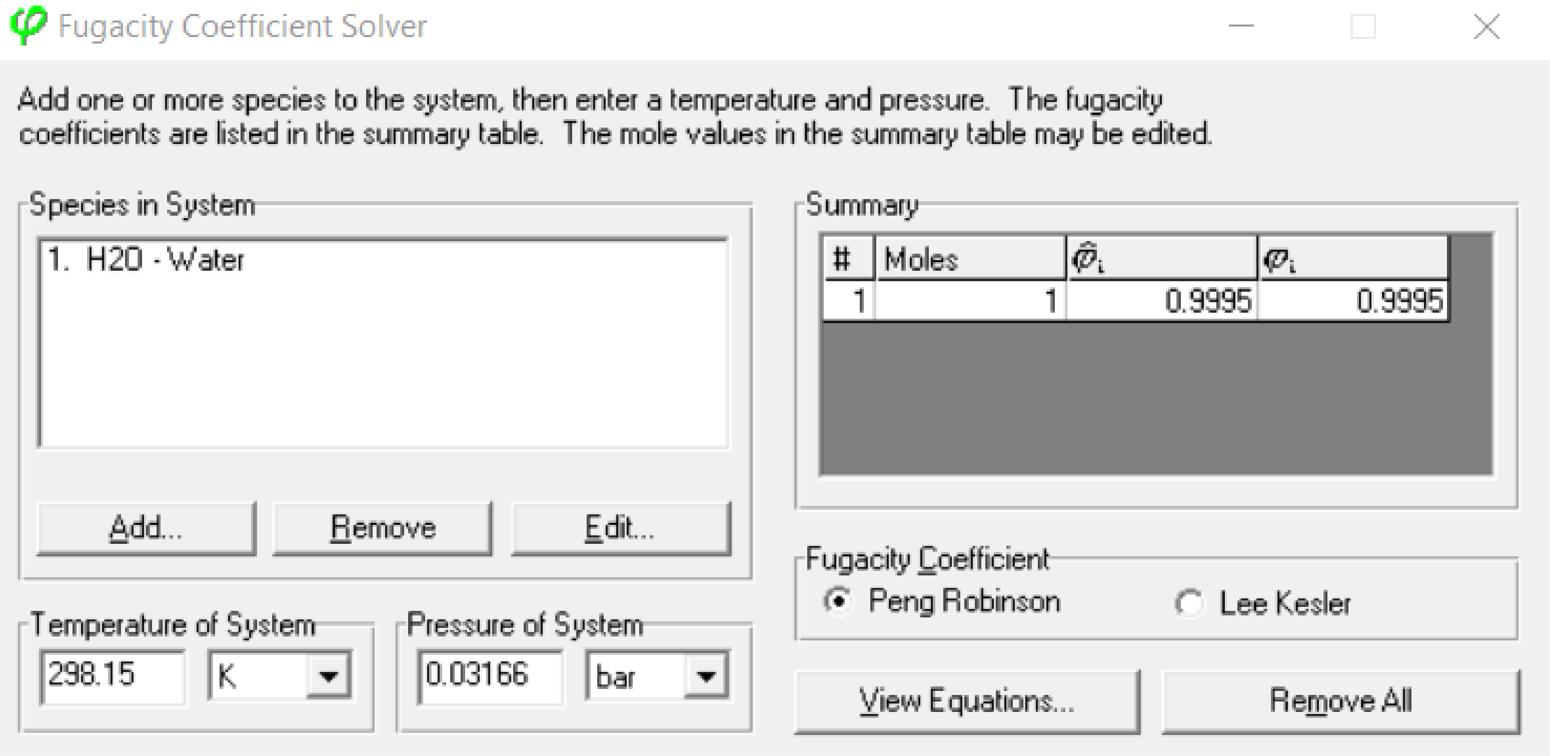
**Solution** The fugacity of the saturated liquid is equal to the fugacity of the saturated vapor

$f_L = f_V = \phi^{sat} P^{sat}$

The saturation pressure at 25 °C is 0.03166 bar and at such low pressure the vapor phase is ideal, that is, $\phi^{sat} \approx 1$. Therefore, the fugacity is equal to the saturation pressure,

$f_L = f_V \approx 0.03166$ bar,

and the fugacity coefficient is 1.



Add one or more species to the system, then enter a temperature and pressure. The fugacity coefficients are listed in the summary table. The mole values in the summary table may be edited.

Species in System

1. H2O - Water

Summary

| # | Moles | $\hat{\varphi}_i$ | $\varphi_i$ |
|---|---|---|---|
| 1 | 1 | 0.9995 | 0.9995 |

Fugacity Coefficient

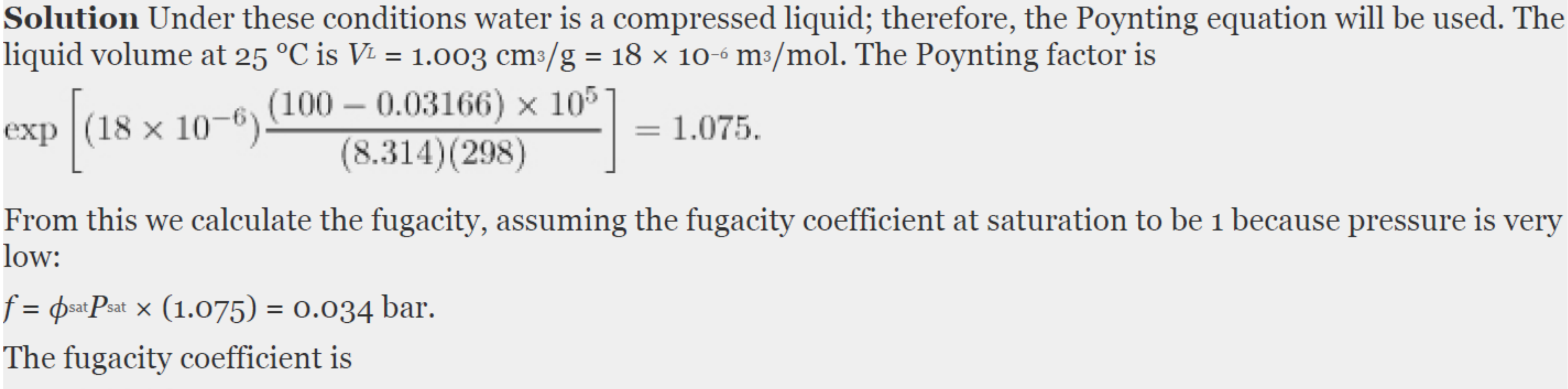
● Peng Robinson ○ Lee Kesler

Temperature of System: 298.15 K

Pressure of System: 0.03166 bar

## Example **7.5-Matsoukas**: Poynting Factor

Calculate the fugacity and fugacity coefficient of water at 25°C, 100 bar, using data from the steam tables.



**Solution** Under these conditions water is a compressed liquid; therefore, the Poynting equation will be used. The liquid volume at 25 °C is $V^L$ = 1.003 $cm^3/g$ = 18 × $10^{-6}$ $m^3/mol$. The Poynting factor is

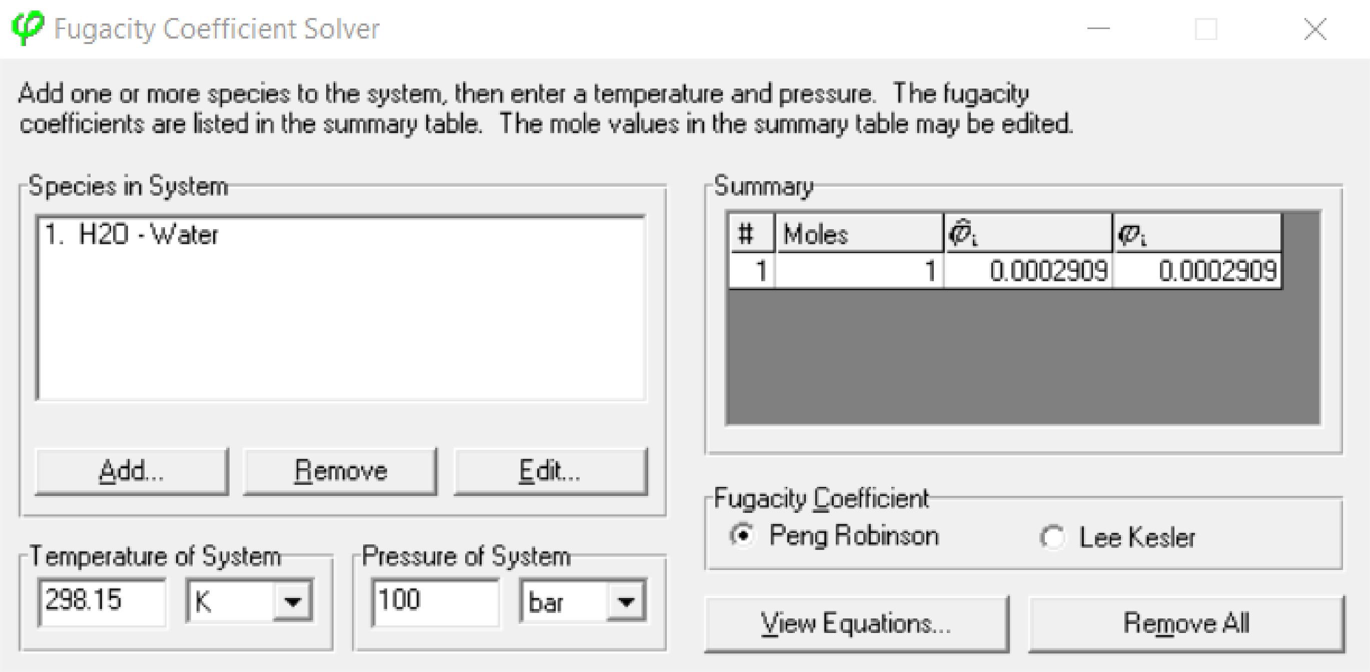
$$\exp\left[(18 \times 10^{-6})\frac{(100 - 0.03166) \times 10^5}{(8.314)(298)}\right] = 1.075.$$

From this we calculate the fugacity, assuming the fugacity coefficient at saturation to be 1 because pressure is very low:

$f = \phi^{sat} P^{sat} \times (1.075) = 0.034$ bar.

The fugacity coefficient is

$$\phi = \frac{0.034 \text{ bar}}{100 \text{ bar}} = 3.4 \times 10^{-4}.$$



Add one or more species to the system, then enter a temperature and pressure. The fugacity coefficients are listed in the summary table. The mole values in the summary table may be edited.

Species in System

1. H2O - Water

Summary

| # | Moles | $\hat{\varphi}_i$ | $\varphi_i$ |
|---|---|---|---|
| 1 | 1 | 0.0002909 | 0.0002909 |

Fugacity Coefficient

● Peng Robinson ○ Lee Kesler

Temperature of System: 298.15 K

Pressure of System: 100 bar

# Calculation of Fugacity Using Tabulated Properties

- Self-read

# Fugacity From Compressibility Factor

- Transform the integration of fugacity to obtain the result:

$$\ln \phi = \int_{P \to 0}^{P} \frac{(Z - 1)}{P} dP$$

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

- Use the truncated virial EOS:

$$Z = 1 + \frac{B(T)P}{RT}$$

$$\ln \phi = Z - 1$$

**Compressibility Factor**
- Experimental
- Tabular
- Equation of State (EOS)

Example **7.7-Matsoukas**: Fugacity of Steam

Estimate the fugacity of steam at 300°C and 70 bar if the only information available is the density of steam at this state, 33.898 kg/m$^3$.

**Solution** We assume that the truncated virial is valid at this state (we will return to this assumption). The molar volume of steam at these conditions is

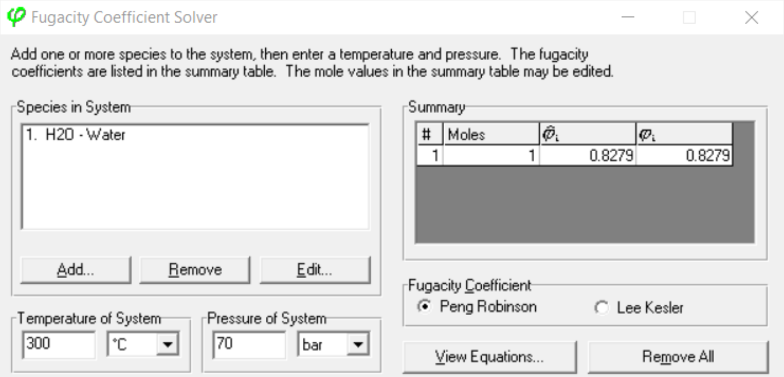
$$V = \frac{1}{33.898} = 0.0295 \text{ m}^3/\text{kg} = 5.314 \times 10^{-4} \text{ m}^3/\text{mol}.$$

The compressibility factor is

$$Z = \frac{(70 \times 10^5 \text{ Pa})(5.314 \times 10^{-4} \text{ m}^3/\text{mol})}{(8.314 \text{ J/mol K})(573.15 \text{ K})} = 0.780685.$$

The fugacity coefficient is

$$\ln \phi = 1 - 0.780685 = -0.219315 \quad \Rightarrow \quad \phi = 0.803$$



Fugacity Coefficient Solver

Add one or more species to the system, then enter a temperature and pressure. The fugacity coefficients are listed in the summary table. The mole values in the summary table may be edited.

Species in System

1. H20 - Water

Summary

| # | Moles | $\hat{\varphi}_i$ | $\varphi_i$ |
|---|---|---|---|
| 1 | 1 | 0.8279 | 0.8279 |

Fugacity Coefficient: ● Peng Robinson ○ Lee Kesler

Temperature of System: 300 °C

Pressure of System: 70 bar

and the fugacity is

*f* = (0.803)(70 bar) = 56.2 bar.

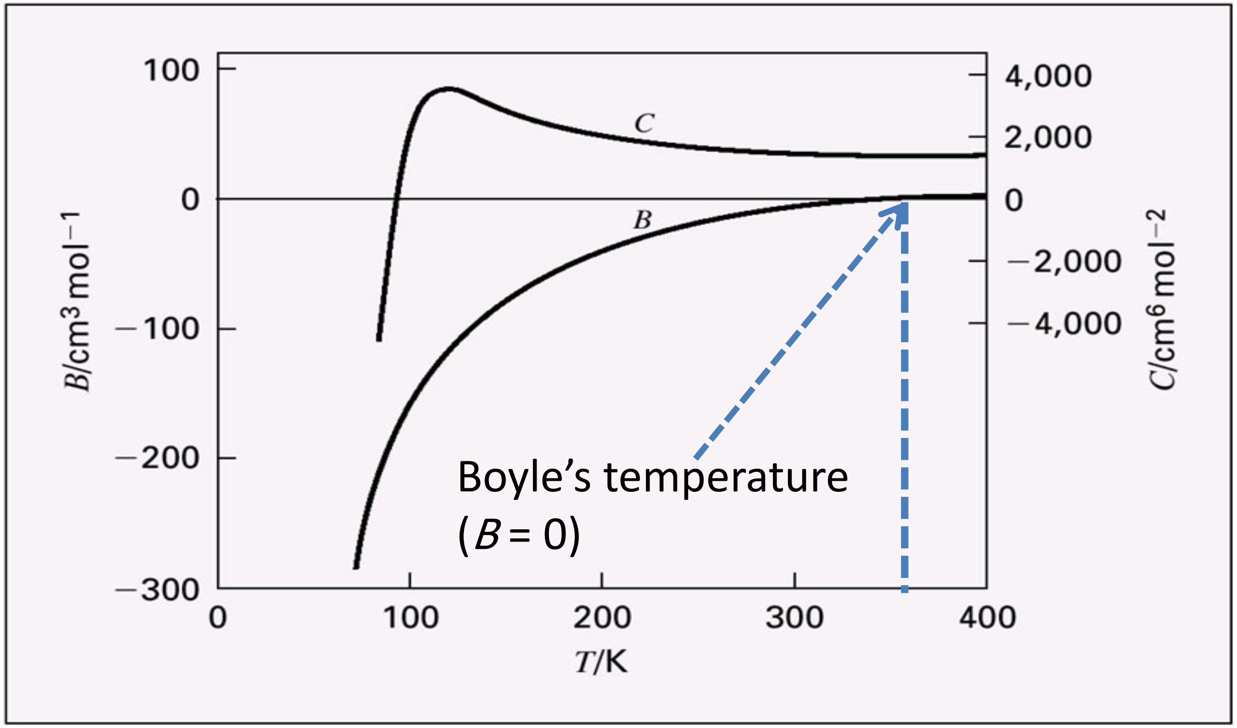
*Comments* To assess the validity of the truncated virial we check with a generalized compressibility chart. The reduced coordinates of water at this state are

$$T_r = \frac{573.15 \text{ K}}{647.096 \text{ K}} = 0.886, \quad P_r = \frac{70 \text{ bar}}{220.64 \text{ bar}} = 0.317.$$

From Figure 2-8 we see that the reduced pressure is fairly low and the isotherm does not exhibit significant nonlinearity. Therefore, the assumption that the isotherm is linear is acceptable. This should be confirmed by an independent calculation of the fugacity from a different method. In Example 7.6 we calculated the fugacity using eq. (7.13) and found *f* = 57.92 bar. The present calculation is within 3% of that value.

# The Virial EOS

- Second virial coefficients are easily obtained in compilations or estimated using Pitzer's Correlation.
- Third virial coefficients and higher are not easily obtained or estimated.
- Virial EOS is usually truncated to the second term.



Boyle's temperature ($B = 0$)

For –ve B: Z < 1 (Attractive forces)
For +ve B: Z > 1 (Repulsive forces)
For Boyle's temperature B = 0 and Z = 1 (Attractive = repulsive forces)

# Pitzer's Correlations for Second Virial Coefficients

- Applies to nonpolar gases

$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B}\,\frac{P_r}{T_r}$$

$$\hat{B} = \frac{BP_c}{RT_c} = B^0 + \omega B^1$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

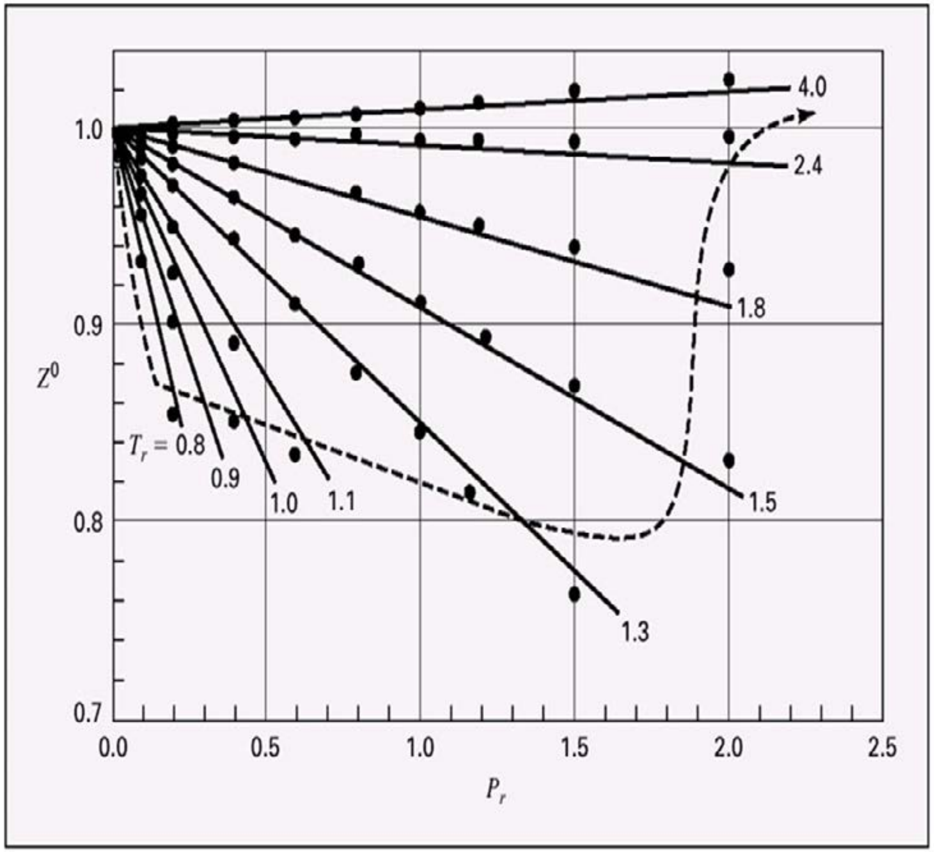
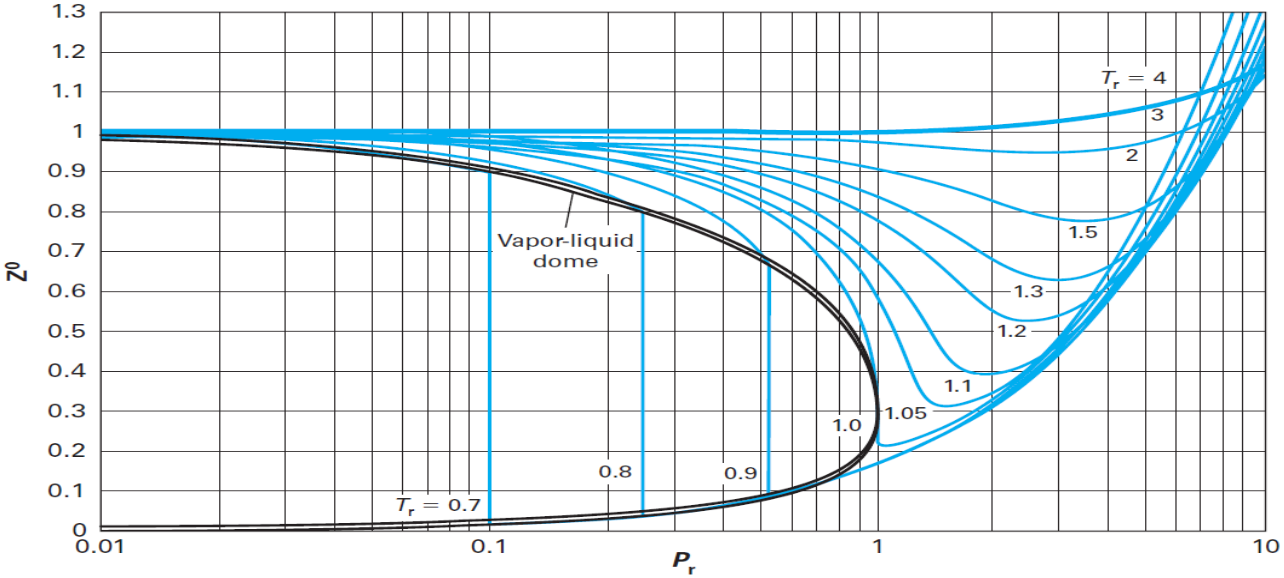


**Figure 3.14**: Comparison of correlations for $Z^0$. The virial-coefficient correlation is represented by the straight lines; the Lee/Kesler correlation, by the points. In the region above the dashed line the two correlations differ by less than 2%.

Example: Estimate the compressibility factor for steam at 300°C and 70 bar. Compare your result to the value given in steam tables at these conditions.

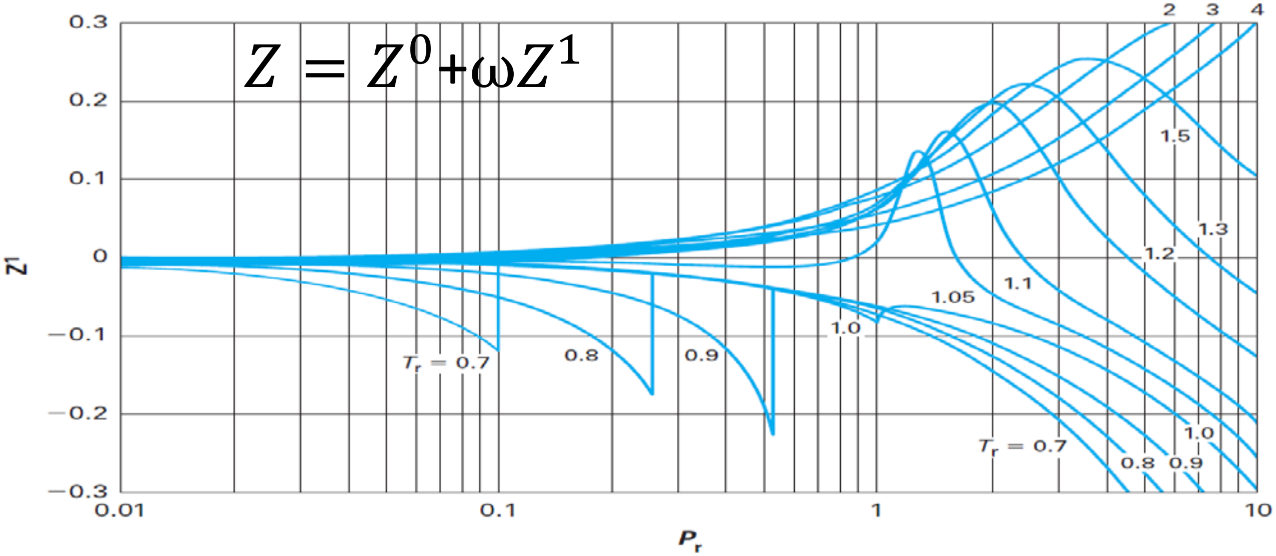
| | | | |
|---|---|---|---|
| w | **0.344** | R (J/mol.K) | **8.314** |
| Tc (K) | **647.3** | T (K) | **573.15** |
| Pc (bar) | **220.48** | P (bar) | **70** |
| | | | |
| Pr | **0.317489** | | |
| Tr | **0.885447** | | |
| | | | |
| B0 | **-0.42969** | | |
| B1 | **-0.14771** | | |
| Bhat | **-0.4805** | | |
| Z | **0.82771** | | |
| B (m3/mol) | **-0.00012** | | |
| V (m3/mol) | **0.000563** | V(m3/kg) | **0.031303** |
| Vsteam (m3/kg) | **0.0442** | | |

# Generalized Compressibility Factor Charts



Based on Lee B.I., Kesler M.G., "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States", AIChE J., 21(3), 510-527, 1975.

**FIGURE 7-14** Compressibility factor for a compound with $\omega = 0$ for use in the Lee-Kesler equation.



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

Based on Lee B.I., Kesler M.G., "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States", AIChE J., 21(3), 510-527, 1975.

**FIGURE 7-15** Compressibility correction factor for a compound with $\omega = 1$ for use in the Lee-Kesler equation.

# Fugacity from Generalized Graphs

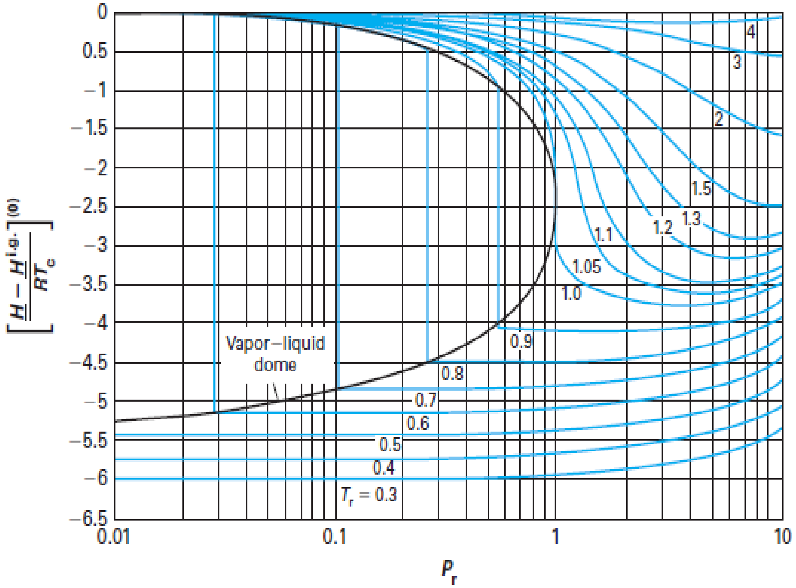
- The residual Gibbs energy can be calculated from the residual enthalpy and entropy.

$$\frac{H^R}{RT_c} = \frac{H^{R,0}}{RT_c} + \omega \frac{H^{R,1}}{RT_c}$$

$$\frac{S^R}{RT_c} = \frac{S^{R,0}}{RT_c} + \omega \frac{S^{R,1}}{RT_c}$$

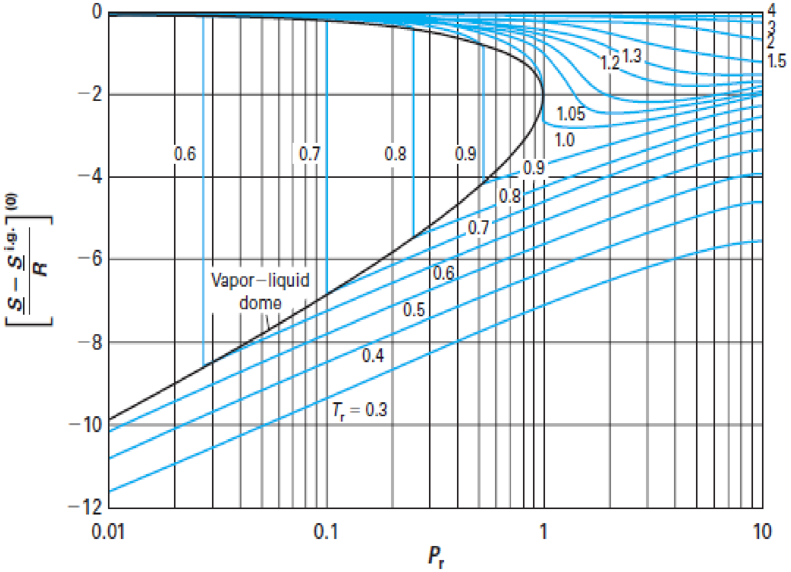
- Charts have been developed to utilize the Lee-Kessler equation of state with corresponding states theory ( reduced units).

$$\ln \phi = \ln \phi^0 + \omega \ln \phi^1$$



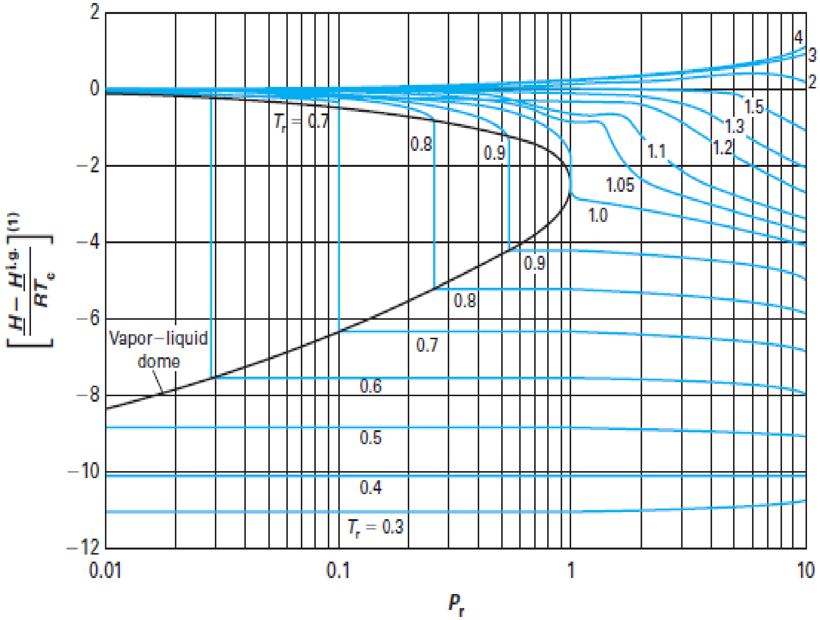
Based on Lee B.I., Kesler M.G., "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States", AIChE J., 21(3), 510-527, 1975.

**FIGURE 7-16** Molar enthalpy residual function for a compound with $\omega = 0$, as determined using the Lee-Kesler equation.



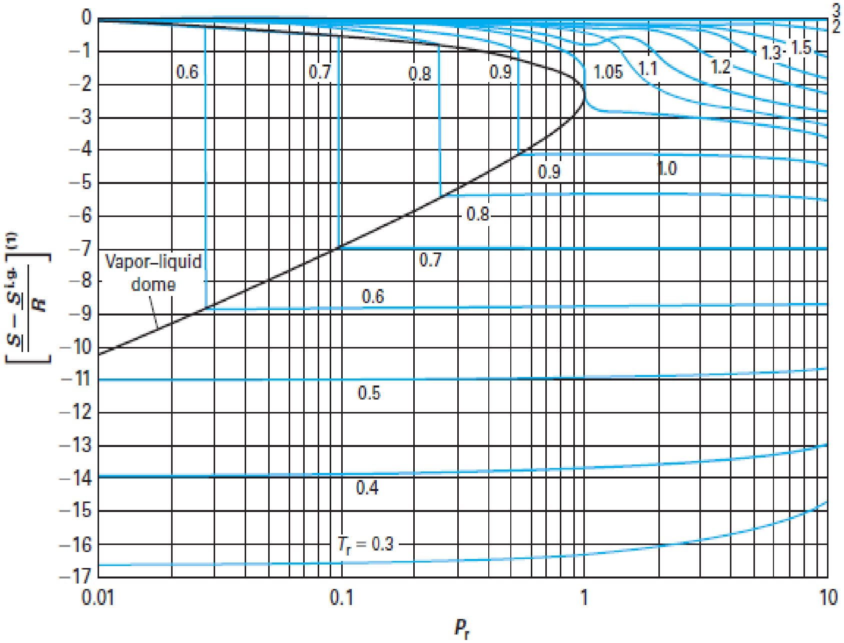
Based on Lee B.I., Kesler M.G., "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States", AIChE J., 21(3), 510-527, 1975.

**FIGURE 7-18** Molar entropy residual function for a compound with $\omega = 0$, as determined using the Lee-Kesler equation.



Based on Lee B.I., Kesler M.G., "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States", AIChE J., 21(3), 510-527, 1975.

**FIGURE 7-17** Correction to the molar enthalpy residual function for a compound with $\omega = 1$, as determined using the Lee-Kesler equation.



Based on Lee B.I., Kesler M.G., "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States", AIChE J., 21(3), 510-527, 1975.

**FIGURE 7-19** Correction to the molar entropy residual function for a compound with $\omega = 1$, as determined using the Lee-Kesler equation.

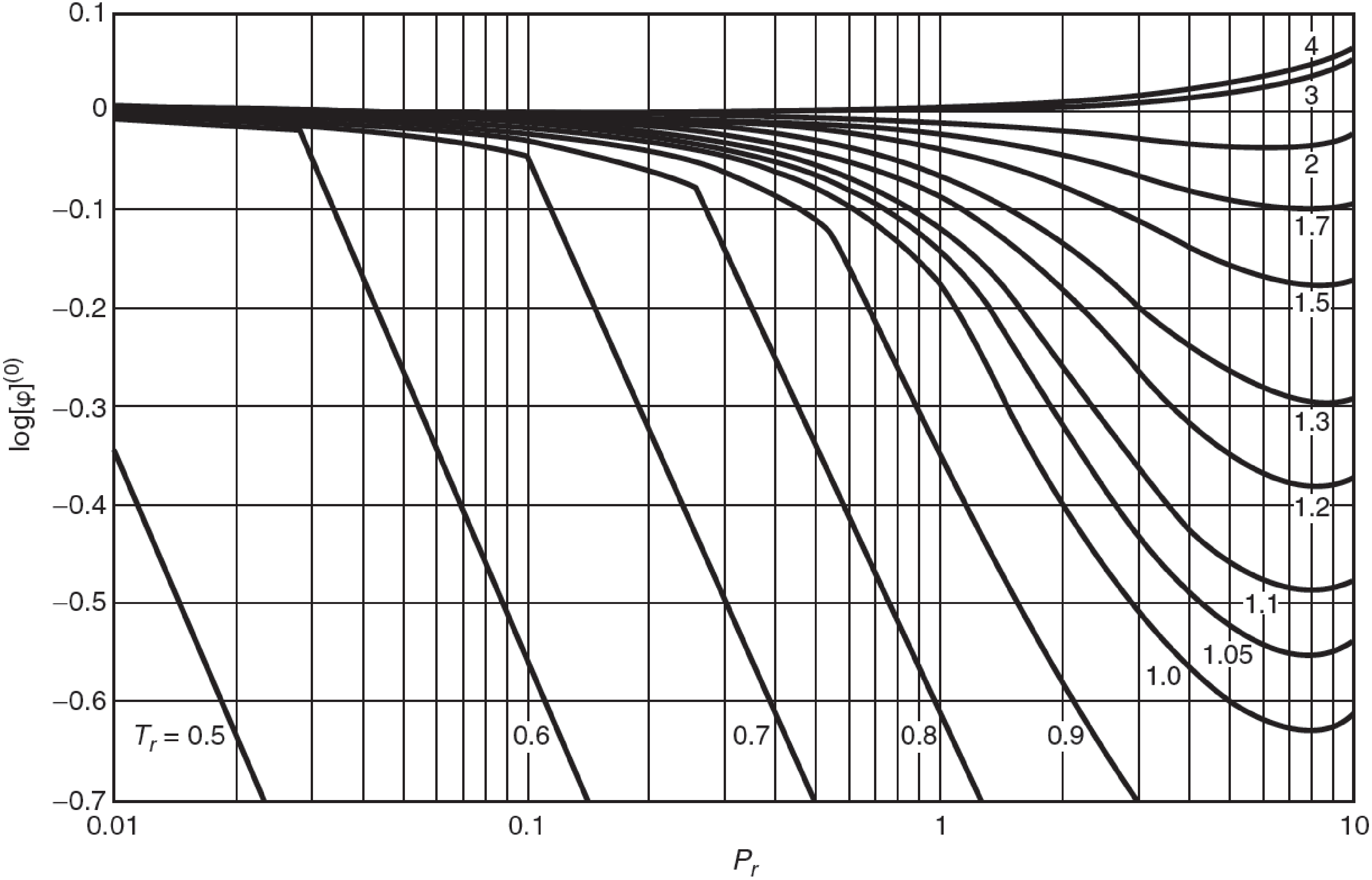


**Figure 7.1** Corresponding states correlation for the fugacity coefficient in reduced coordinates—simple fluid term. Based on the Lee–Kesler equation of state.

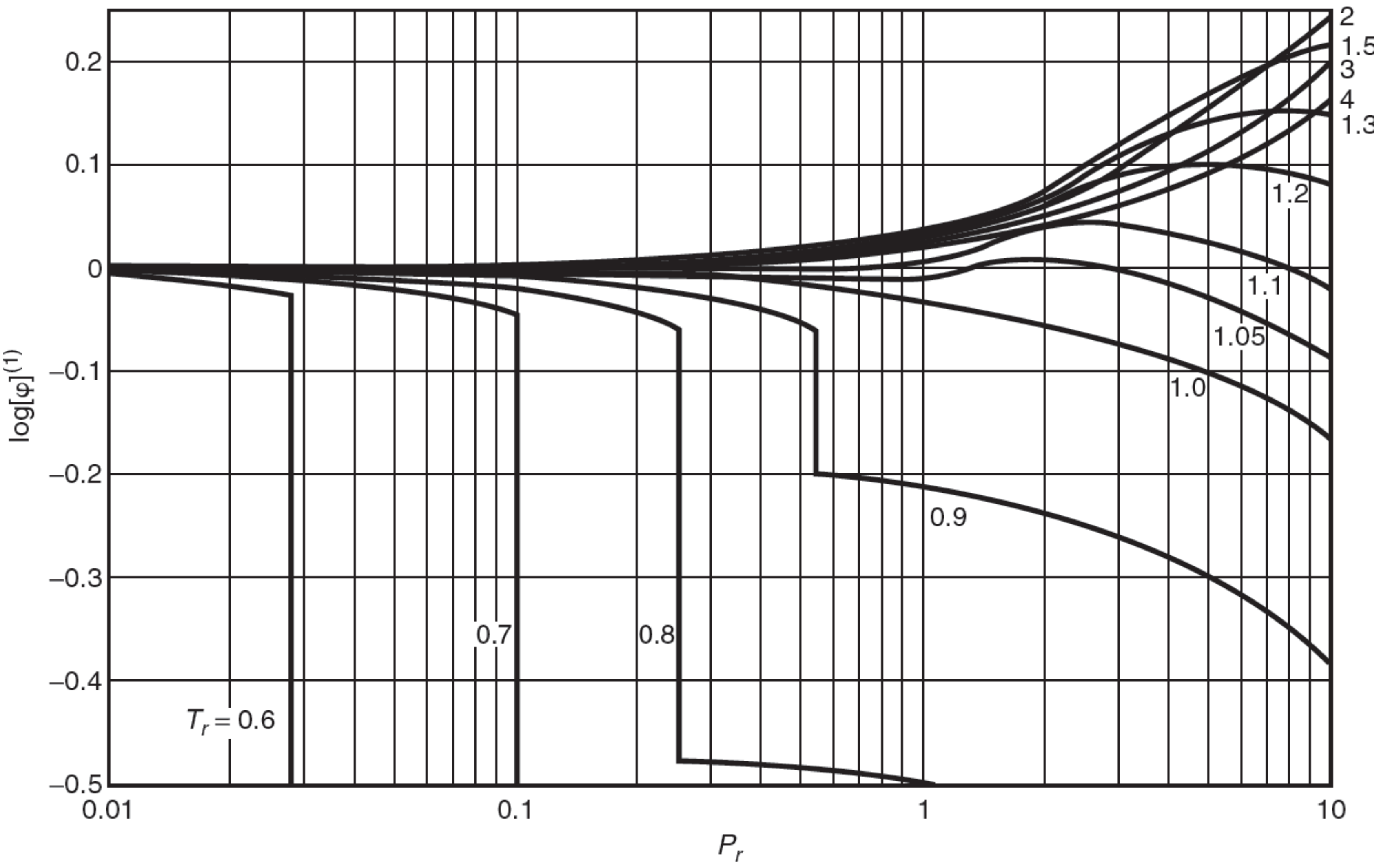
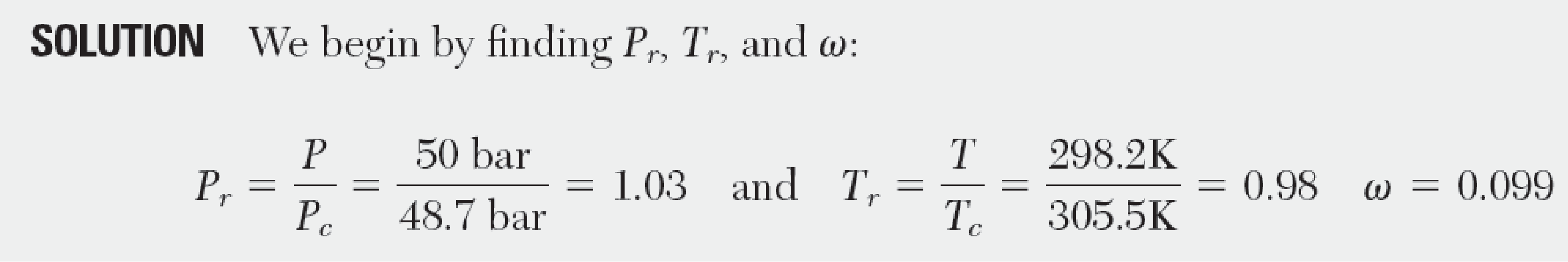


**Figure 7.2** Corresponding states correlation for the fugacity coefficient in reduced coordinates—correction term. Based on the Lee–Kesler equation of state.

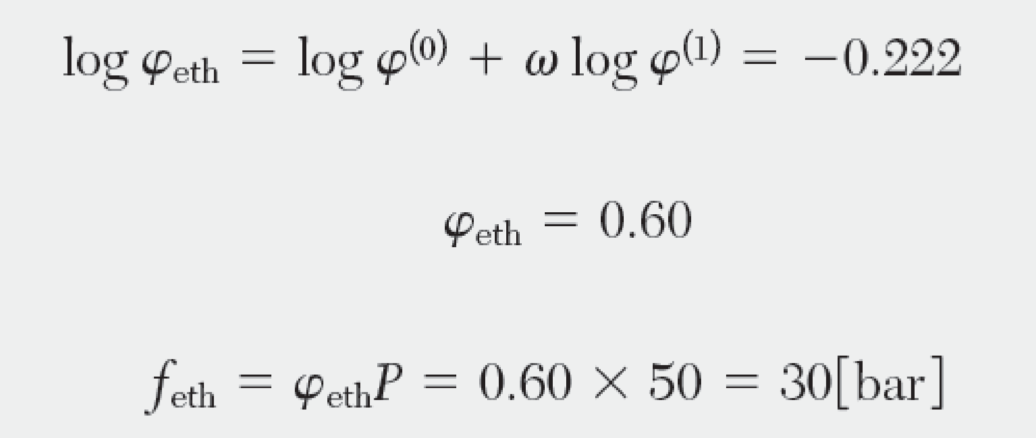
**Example 7.13-Kortesky** Determine the fugacity and the fugacity coefficient of ethane at a pressure of 50 bar and a temperature of 25°C using generalized correlations.



**SOLUTION** We begin by finding $P_r$, $T_r$, and $\omega$:

$$P_r = \frac{P}{P_c} = \frac{50\text{ bar}}{48.7\text{ bar}} = 1.03 \quad \text{and} \quad T_r = \frac{T}{T_c} = \frac{298.2\text{K}}{305.5\text{K}} = 0.98 \quad \omega = 0.099$$

$$\ln \phi^0\text{=-0.216} \qquad \ln \phi^1\text{=-0.060}$$



$$\log \varphi_{\text{eth}} = \log \varphi^{(0)} + \omega \log \varphi^{(1)} = -0.222$$

$$\varphi_{\text{eth}} = 0.60$$

$$f_{\text{eth}} = \varphi_{\text{eth}} P = 0.60 \times 50 = 30[\text{bar}]$$

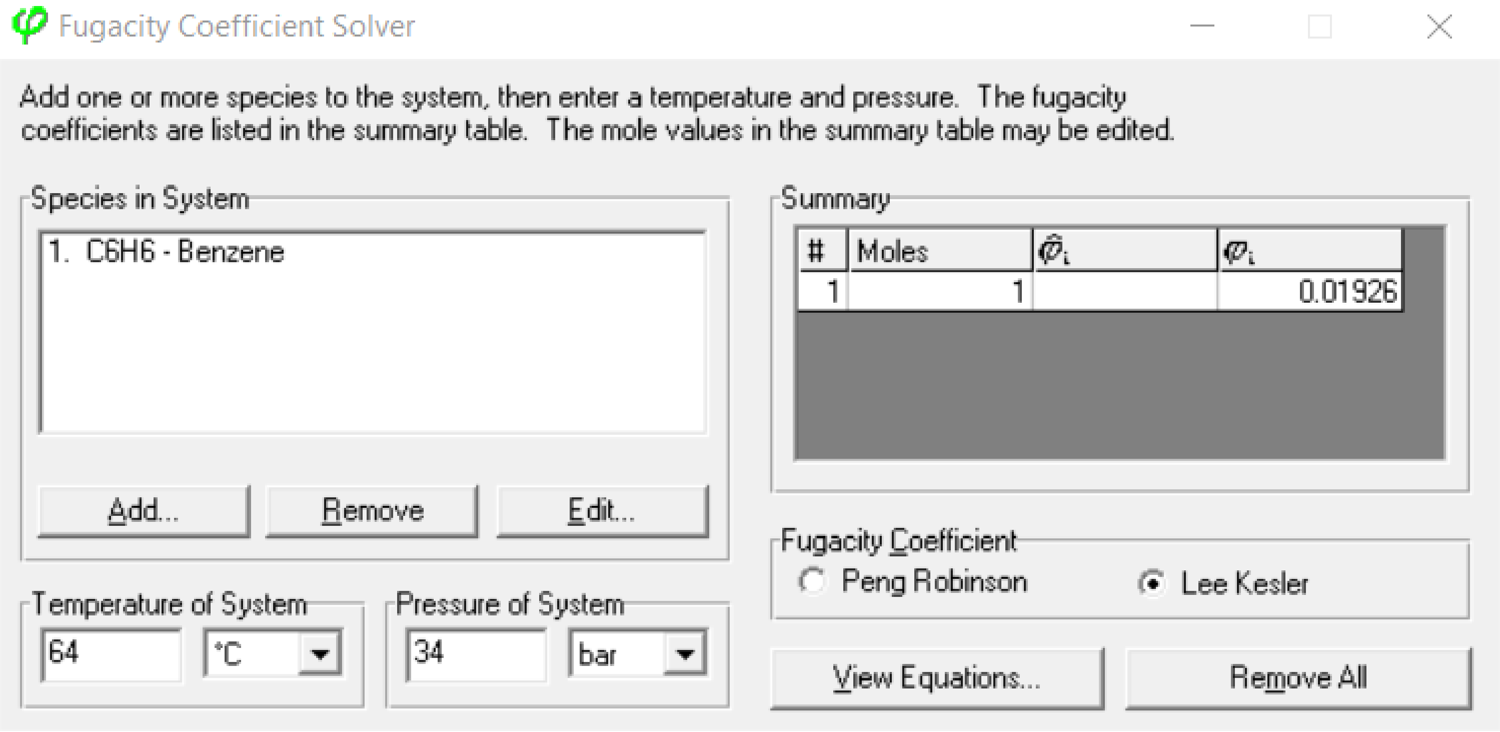
there are significant deviations from ideality. Since $\phi$<1, we surmise that attractive forces dominate. This result is expected since the system is around the critical point of ethane, where intermolecular interactions are large.

**Example 7.8-Matsoukas**: Calculate the fugacity of benzene at T = 64°C, P = 34 bar using the Lee-Kesler method.

**Solution** With $T_c = 562.1$ K, $P_c = 48.9$ bar, the given conditions correspond to $T_r = 0.6$, $P_r = 0.7$. From tables E13, E15, we find by interpolation, $\phi^0 = 0.04415$, $\phi^1 = 0.02145$. Notice that these values are printed in italics indicating that the state is liquid. The fugacity coefficient is

$$\phi = (0.04415)(0.02145)^{0.210} = 0.0197$$

and the fugacity is $f = \phi P = (0.0197)(34) = 0.67$ bar.



Fugacity Coefficient Solver

Add one or more species to the system, then enter a temperature and pressure. The fugacity coefficients are listed in the summary table. The mole values in the summary table may be edited.

Species in System

1. C6H6 - Benzene

Summary

| # | Moles | $\hat{\varphi}_i$ | $\varphi_i$ |
|---|---|---|---|
| 1 | 1 | | 0.01926 |

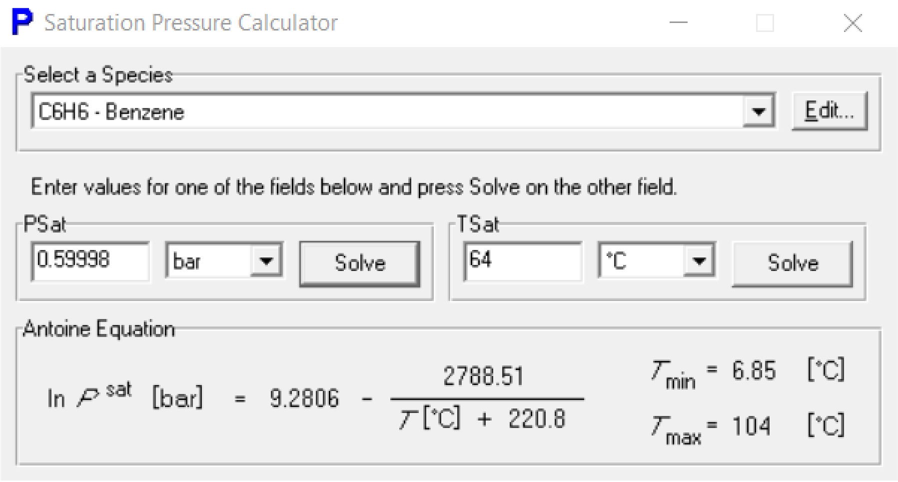
Temperature of System: 64 °C

Pressure of System: 34 bar

Fugacity Coefficient

○ Peng Robinson ● Lee Kesler

# **Example 7.8-Matsoukas**: alternate solution using Poynting method



Select a Species: C6H6 - Benzene

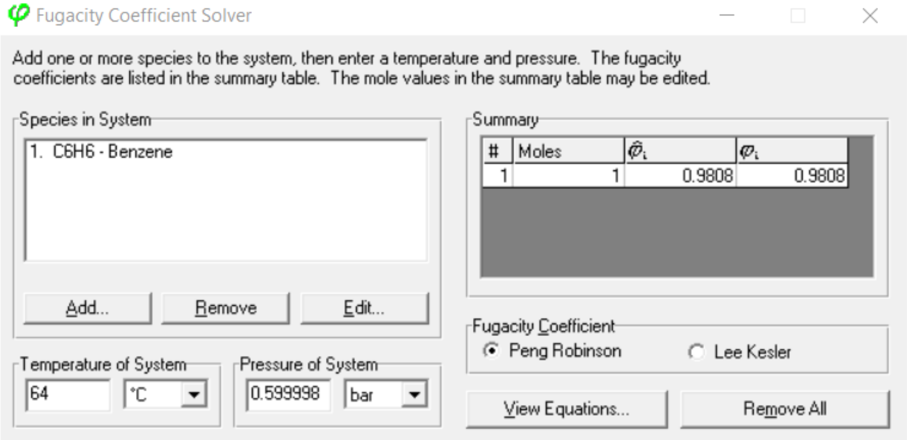
Enter values for one of the fields below and press Solve on the other field.

PSat: 0.59998 bar

TSat: 64 °C

Antoine Equation

$$\ln P^{\text{sat}}\ [\text{bar}] = 9.2806 - \frac{2788.51}{T\,[^\circ\text{C}] + 220.8} \qquad T_{\min} = 6.85\ [^\circ\text{C}] \qquad T_{\max} = 104\ [^\circ\text{C}]$$



Add one or more species to the system, then enter a temperature and pressure. The fugacity coefficients are listed in the summary table. The mole values in the summary table may be edited.

Species in System: 1. C6H6 - Benzene

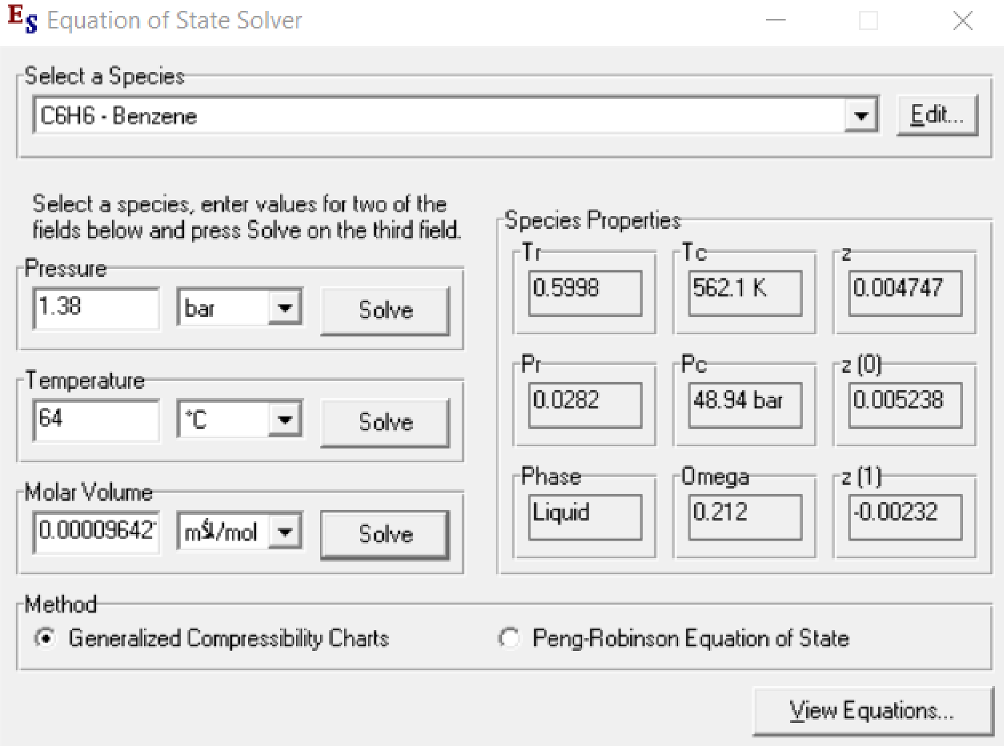
Summary

| # | Moles | $\hat{\varphi}_i$ | $\varphi_i$ |
|---|---|---|---|
| 1 | 1 | 0.9808 | 0.9808 |

Fugacity Coefficient: ● Peng Robinson ○ Lee Kesler

Temperature of System: 64 °C

Pressure of System: 0.599998 bar



Select a Species: C6H6 - Benzene

Select a species, enter values for two of the fields below and press Solve on the third field.

Pressure: 1.38 bar

Temperature: 64 °C

Molar Volume: 0.00009642 m³/mol

Species Properties

| | | |
|---|---|---|
| Tr: 0.5998 | Tc: 562.1 K | z: 0.004747 |
| Pr: 0.0282 | Pc: 48.94 bar | z (0): 0.005238 |
| Phase: Liquid | Omega: 0.212 | z (1): -0.00232 |

Method: ● Generalized Compressibility Charts ○ Peng-Robinson Equation of State

$$f\,(T,P) = \phi^{\text{sat}}(T,P^{\text{sat}})P^{\text{sat}}(T)\exp\left[\frac{(P-P^{\text{sat}})}{RT}V_L\right]$$

$$= 0.9808(0.599998)\exp\left[\frac{(34-0.599998)\times 10^5}{8.314(64+273.15)}(0.00009642)\right]$$

$$= 0.9808(0.599998)(1.1217) = 0.6601\text{bar}$$

# Fugacity from Cubic Equations of State

- Convert the integration from volume explicit to pressure explicit to obtain:

$$\ln\phi = \ln\frac{f(T,P)}{P} = \frac{1}{RT}\left[\int_{v=\infty}^{v}\left(\frac{RT}{v} - P\right)dv\right] - \ln Z + (Z-1)$$

**Soave-Redlich-Kwong (SRK)**

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}$$

$$a(T) = 0.42748\frac{(RT_c)^2}{P_c}\alpha(T)$$

$$\sqrt{\alpha(T)} = 1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)$$

$$\kappa = 0.480 + 1.57\omega - 0.176\omega^2$$

$$b = 0.08664\frac{RT_c}{P_c}$$

**Peng-Robinson (PR)**

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)}$$

$$a(T) = 0.45724\frac{(RT_c)^2}{P_c}\alpha(T)$$

$$\sqrt{\alpha(T)} = 1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)$$

$$\kappa = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

$$b = 0.07779\frac{RT_c}{P_c}$$

# Cubic EOS Coefficients in Compressibility Form

$$Z^3 + a_2 Z^2 + a_1 Z + a_0 = 0$$

| | vdW | SRK | PR |
|---|---|---|---|
| $a_2$ | $-1 - B'$ | $-1$ | $-1 + B'$ |
| $a_1$ | $A'$ | $A' - B' - B'^2$ | $A' - 2B' - 3B'^2$ |
| $a_0$ | $-A'B'$ | $-A'B'$ | $-A'B' + B'^2 + B'^3$ |
| $Z_c$ | 0.3750 | 0.3333 | 0.3074 |

$$A' = \frac{aP}{(RT)^2} \qquad B' = \frac{bP}{RT}$$

**Initial Guess for solution**

**Vapor (Vapor like): ideal gas ($Z = 1$).**

**Liquid: Reduced covolume ($Z = B'$).**

# Solution Methodology for SRK EOS

1. Obtain ($T_c$;$P_c$;$\omega$).

2. Find $b$ in SRK EOS.

$$b = 0.08664\frac{RT_c}{P_c}$$

3. Find $a$ in SRK EOS

- Determine $\kappa$.
- Determine $\alpha$.
- Determine $a(T)$.

$$\kappa = 0.480 + 1.57\omega - 0.176\omega^2$$

$$\sqrt{\alpha(T)} = 1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)$$

$$a(T) = 0.42748\frac{(RT_c)^2}{P_c}\alpha(T)$$

4. Determine reduced parameters $A'$ and $B'$.

$$A' = \frac{aP}{(RT)^2} \qquad B' = \frac{bP}{RT}$$

5. Evaluate the cubic constants in the $Z$ expression.

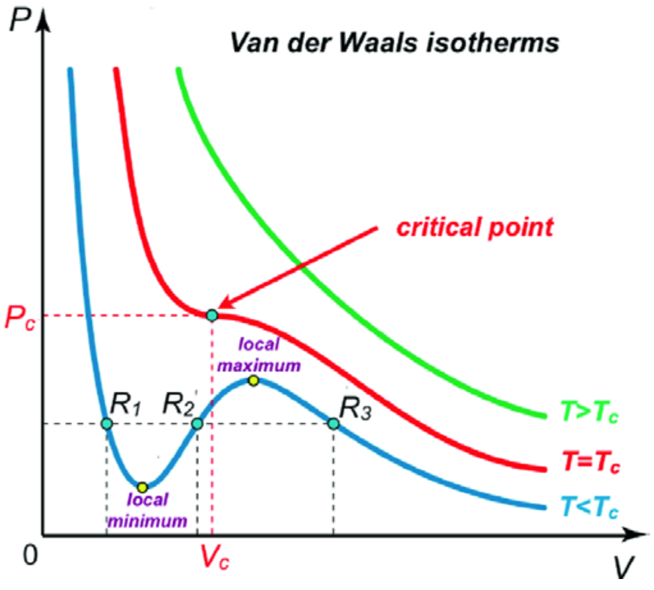
| SRK | |
|---|---|
| $a_2$ | $-1$ |
| $a_1$ | $A' - B' - B'^2$ |
| $a_0$ | $-A'B'$ |

$$Z^3 + a_2 Z^2 + a_1 Z + a_0 = 0$$

6. Solve the cubic for the roots and determine if they fall in the subcooled liquid, superheated vapor, supercritical or the two phase coexistence region.

# Roots of a Cubic

- Roots of cubic EOS
  - $T > T_c$
    - One real root (molar volume of supercritical fluid)
    - Two negative or conjugate complex roots with no physical significance)
  - $T = T_c$
    - Three equal real roots representing molar volume of the critical fluid.
  - $T < T_c$
    - Maximum positive root for vapor molar volume
    - Minimum positive real root for liquid molar volume if > B
    - Intermediate real root for spinodal or **metastable** limits.



# Fugacity Expressions for PR and SRK EOS

- SRK

$$\ln\frac{f}{P}=(Z-1)-\ln\left(Z-B'\right)-\frac{A'}{B'}\ln\left[\frac{Z+B'}{Z}\right]$$

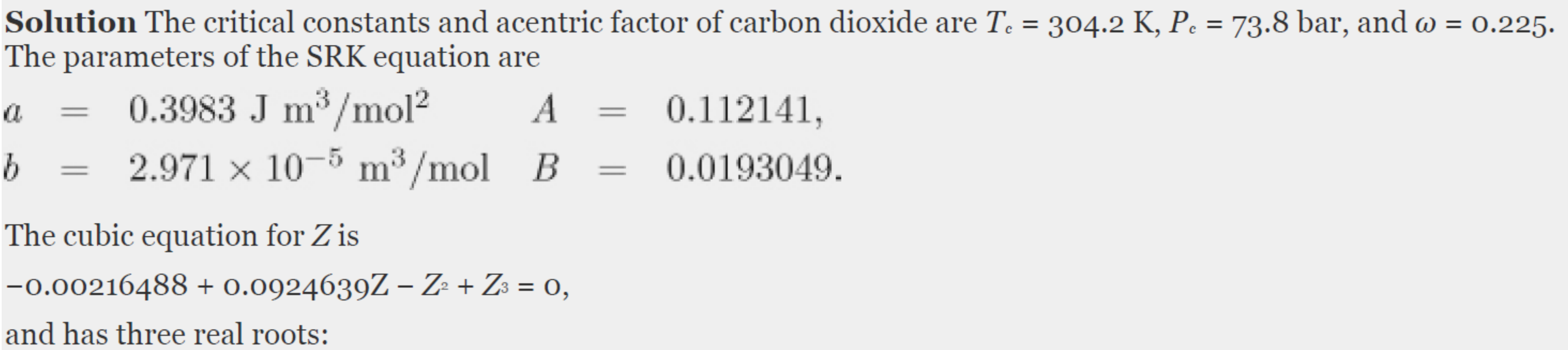
- PR

$$\ln\frac{f}{P}=(Z-1)-\ln\left(Z-B'\right)-\frac{A'}{2\sqrt{2}B'}\ln\left[\frac{Z+(1+\sqrt{2})B'}{Z+(1-\sqrt{2})B'}\right]$$

- Requires the compressibility factor at the pressure and temperature of interest.
- If the polynomial equation for *Z* has three real roots, the proper root must be selected based on the phase of the
- system.

# Example 7.9-Matsoukas: Fugacity from the SRK

Calculate the fugacity of $CO_2$ vapor at 4.5°C, 15 bar, using the SRK equation.



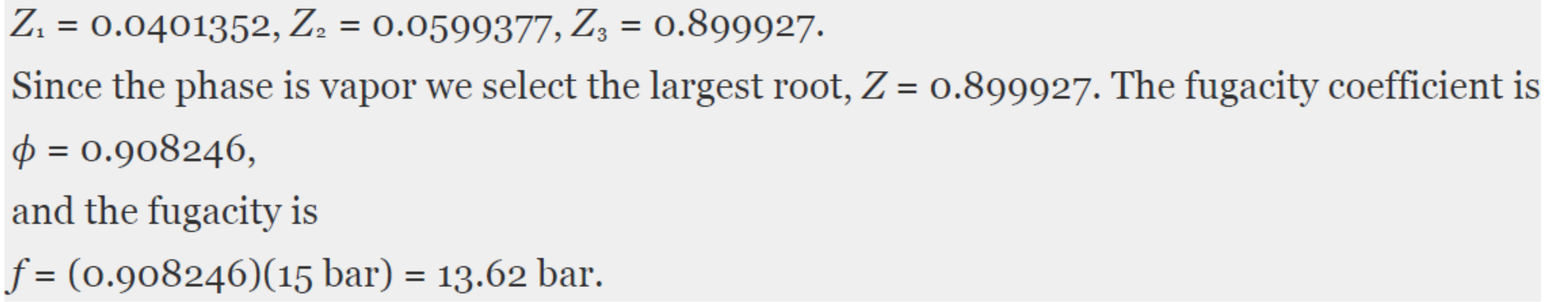
**Solution** The critical constants and acentric factor of carbon dioxide are $T_c = 304.2$ K, $P_c = 73.8$ bar, and $\omega = 0.225$. The parameters of the SRK equation are

$$\begin{aligned} a &= 0.3983\ \mathrm{J\ m^3/mol^2} & A &= 0.112141, \\ b &= 2.971 \times 10^{-5}\ \mathrm{m^3/mol} & B &= 0.0193049. \end{aligned}$$

The cubic equation for $Z$ is

$$-0.00216488 + 0.0924639Z - Z^2 + Z^3 = 0,$$

and has three real roots:



$Z_1 = 0.0401352$, $Z_2 = 0.0599377$, $Z_3 = 0.899927$.

Since the phase is vapor we select the largest root, $Z = 0.899927$. The fugacity coefficient is

$$\phi = 0.908246,$$

and the fugacity is

$$f = (0.908246)(15\ \text{bar}) = 13.62\ \text{bar}.$$

# Effect of *T* and *P* on the Fugacity

- The effect of temperature and pressure upon the fugacity can be derived and are given by:

$$RT\left(\frac{\partial \ln f(T,P)}{\partial P}\right)_T = v = \left(\frac{\partial g}{\partial P}\right)_T$$

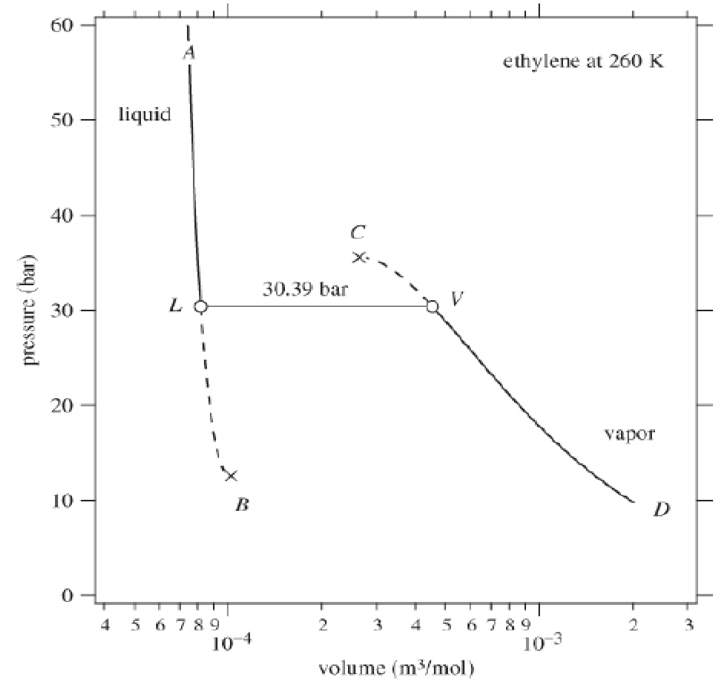
$$\left(\frac{\partial\left[\ln f(T,P)/P\right]}{\partial T}\right)_P = -\frac{h(T,P)-h^{IG}(T,P)}{RT^2}$$

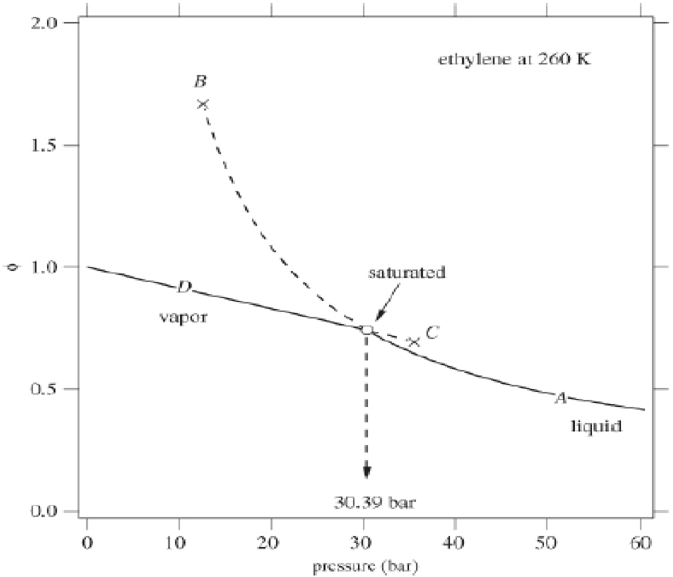
# Saturation Pressure from Equations of State

- For phase equilibrium in a single-phase system; the equilibrium criterion establishes the relationship between pressure and temperature at saturation:

$$\phi^V(T, P^{\text{sat}}) = \phi^L(T, P^{\text{sat}})$$

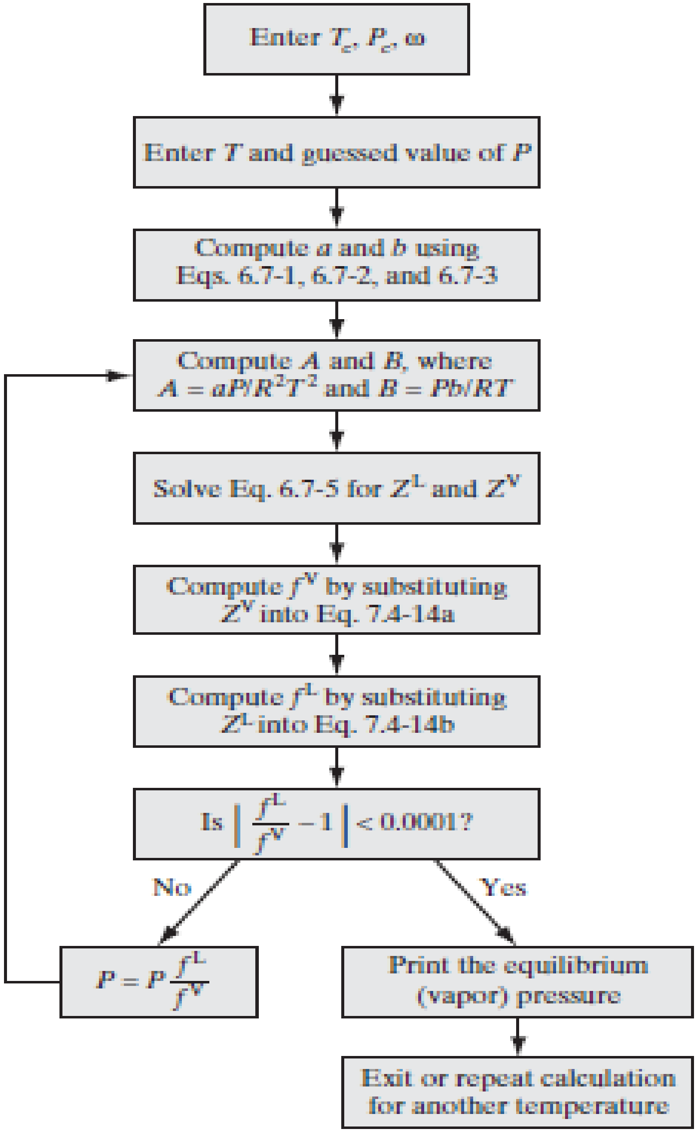
- This equation can be solved for $P^{\text{sat}}$ by trial and error.
- $P^{\text{sat}}$ is defined below $T_c$.





# Algorithm

- Numerically, we seek a pressure such that the fugacity coefficients at $L$ and $V$ are the same.
- This may be done by trial and error.
  - Guess a pressure and solve for the compressibility factor.
  - In this region, there are always three real roots.
  - The smallest root to calculate the fugacity coefficient of the liquid and the largest root to calculate the fugacity coefficient of the vapor.
  - If the two fugacity coefficients are not equal, we pick another pressure and repeat until $\phi^L$ and $\phi^V$ agree to within an acceptable tolerance.



*From Sandler, page 323.*

# Phase Diagrams from Equations of State

- To obtain the properties of a pure fluid at any prescribed T and P, we need
  - An equation of state
  - The ideal-gas heat capacity as a function of temperature.
- The equation of state allows the calculation of:
  - all residual properties and
  - the determination of the phase boundary, namely of the saturation pressure and the properties of the saturated phases.
- Thus we have the tools to compute the entire phase diagram of the pure fluid.

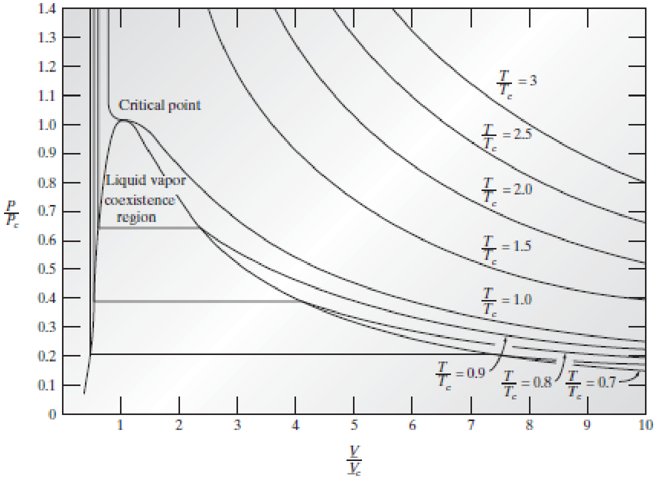


**Figure 7.3-4** The van der Waals fluid with the vapor-liquid coexistence region identified.

*From Sandler, page 304.*

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# References

- Expanded from §7.3 and §7.4: Matsoukas, Themis. Fundamentals of chemical engineering thermodynamics. Pearson Education, 2013.
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- Koretsky, Milo D. Engineering and chemical thermodynamics. John Wiley & Sons, 2012.