Equations of State and Intermolecular Forces

Chapter-4

What is an Equation of State EOS?

Experiment → Measure intensive thermodynamic properties (P, v, T)

↓

Table, diagrams, etc. such as **steam tables**

- Equations of State (EOS): Relate any three intensive, thermodynamic variables.
  - $v = f(T, P)$
  - $P = f(T, v)$
- Such an equation is fit to experimental data and is known as an equation of state since it allows us to calculate the unknown measured property from the two that constrain the state.

We can express EOS in terms of dimensionless compressibility factor:
Define compressibility factor, Z

$$\boxed{Z = \frac{Pv}{RT} = f(T, v) = f(T, P)}$$

- The most common EOS is the ideal gas model:

$$Z = \frac{Pv}{RT} = 1$$

  - Assumptions:
    - Molecules occupy no volume
    - No intermolecular forces is present

- When Does it Apply?
  - Gas only (no condensed phases – liquid or solid)
  - High temperature
  - Low pressure
  - Rule of thumb at P<10 bar

Limitations of Ideal Gas Law

- IGL is a very limited EOS
- Major assumptions of IGL
  - Molecules occupy no volume (good approximation in the limit of $V = \infty$)
  - Molecules exert no intermolecular forces (good approximation if molecules infinitely apart)

- We need something better for dense gases, liquids, etc. where molecules are closer together, so we should account for:
  - Volume will matter
  - Energy of interaction will matter

In order to address the above criteria we should study the interaction between molecules in a substance and the imposed intermolecular forces!

Intermolecular Forces

- Why do some solids dissolve in water but others do not?
- Why are some substances gases at room temperature, but others are liquid or solid?
- What gives metals the ability to conduct electricity?

➢ The answers have to do with …

Intermolecular forces

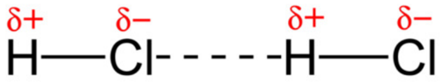
- Generally the potential energy of the molecules can be divided to:
  - Intramolecular potential energy:
    resulted from the covalent bonds that hold the atoms making up a molecule
  - Intermolecular potential energy:
    Results from the interaction between different molecules: attraction vs. repulsion

Intermolecular Forces

Attractive Forces

1. Dipole–Dipole Forces

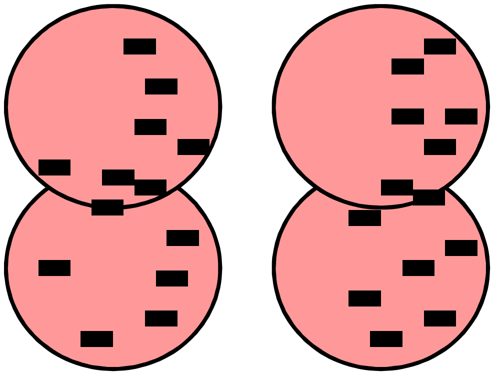
Dipole–dipole interactions are electrostatic interactions of permanent dipoles in molecules. These interactions tend to align the molecules to increase the attraction.



$$\overset{\delta+}{H}-\overset{\delta-}{Cl}\cdots\overset{\delta+}{H}-\overset{\delta-}{Cl}$$

2. London Dispersion Forces

Due to the movement of the electrons in interacting molecules, the electrons, which belong to different molecules, start "feeling" and avoiding each other at the short intermolecular distances. This forms "instantaneous dipoles" that attract each other:

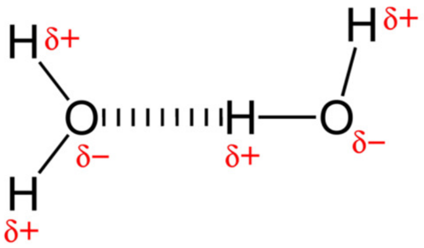


3. Induction Forces

These can occur when one molecule with a permanent dipole repels another molecule's electrons, "inducing" a dipole in that molecule.

4. Hydrogen Bonding

A hydrogen bond is the attractive force between an electronegative atom and a hydrogen atom that is bonded to either nitrogen, oxygen, or fluorine.



Repulsive Forces

Molecules get so close that their electron clouds overlap, leading to a repulsive force.

Principle of Corresponding States

- There are various classes of molecules based on the intermolecular interactions (polarity etc.) and shape. These different classes behave differently. The question is how to study all these different classes of molecules???

➢ Principle of corresponding states:

- Indicates that all non-polar fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor and all deviate from ideal gas behaviour to about the same degree.

The reduced properties are defined as the actual property divided by the critical property:

$$P_r = \frac{P}{P_c} \qquad T_r = \frac{T}{T_c} \qquad v_r = \frac{v}{v_c}$$

➢ What about other classes of molecules?

- We can introduce specific parameters for each of these different classes. One of the most well-known parameters is Pitzer acentric factor, ω, which accounts for the sphericity of the molecules:

$$\boxed{\omega \equiv -1 - \log_{10}\left[P^{sat}(T_r = 0.7)/P_c\right]}$$

$\omega=0$ for simple fluids such as *Ar, Kr,* and *Xe.* For others ω is less than one and is summarized in appendix A-1.

Equations of State

- **Van der Waals Equation:**

- We need to account for the volume of the molecules, thus introduce “b”.
- We need to account for the attractive forces by correcting the pressure. Why? The attractive forces decrease the pressure, since the molecules will not bang into the container as readily, thus introduce “a/v^2”.

$$\boxed{P = \frac{RT}{v-b} - \frac{a}{v^2}}$$

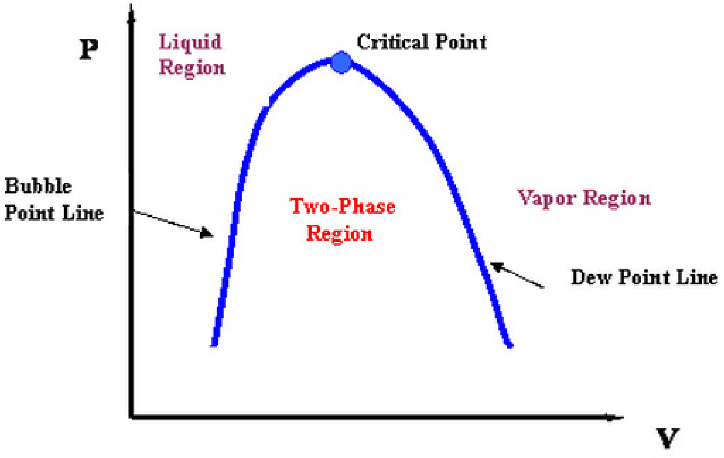
Unoccupied molar volume

- Captures two basic types of physical forces:
  - Attractive (a/v^2)
  - Repulsive (v-b)

“a” and “b”=???

Van der Waals EOS

- At critical point on a *P*-*v* diagram:
  - Slope =0 → $\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0$
  - An inflection point → $\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0$



$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 = \frac{-RT_c}{(v_c - b)^2} + \frac{2a}{v_c^{\ 3}} \qquad (1)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^{\ 4}} \qquad (2)$$

→

Multiply eq.(1) by 2 and eq.(2) by (v_c-b) and add together

↓

$$0 = \frac{4a}{v_c^{\ 3}} - \frac{6a(v_c - b)}{v_c^{\ 4}}$$

$$v_c = 3b \qquad (3)$$

Plug eq. (3) back into eq. (1) and solve for "*a*": $a = \frac{9}{8} R T_c v_c$ (4)

Plug eqn. (4) back into vdw-EOS at critical point

$$P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^{\,2}}$$

Solve for *a* and *b* in terms of T_c and P_c →

$$\boxed{a = \frac{27}{64} \frac{(RT_c)^2}{P_c}}$$

$$\boxed{b = \frac{RT_c}{8P_c}}$$

This EOS predicts Z_c=0.375 instead of 0.29! Better than Ideal gas law not yet perfect!

Van der Waals EOS is a cubic equation of state since there are three roots for volume:

$$Pv^3 - (RT + Pb)v^2 + av - ab = 0$$

- Above the critical point: There is only one positive, real root corresponding to the volume of the supercritical fluid.
- Below the critical point: The highest root is the molar volume of the vapor and the lowest root is the molar volume of the liquid state.

Cubic Equations of State

- More accurate recent EOS will be presented here. The EOS can be described as the general form of:

$$P = \frac{RT}{v - b} - \text{Attr}$$

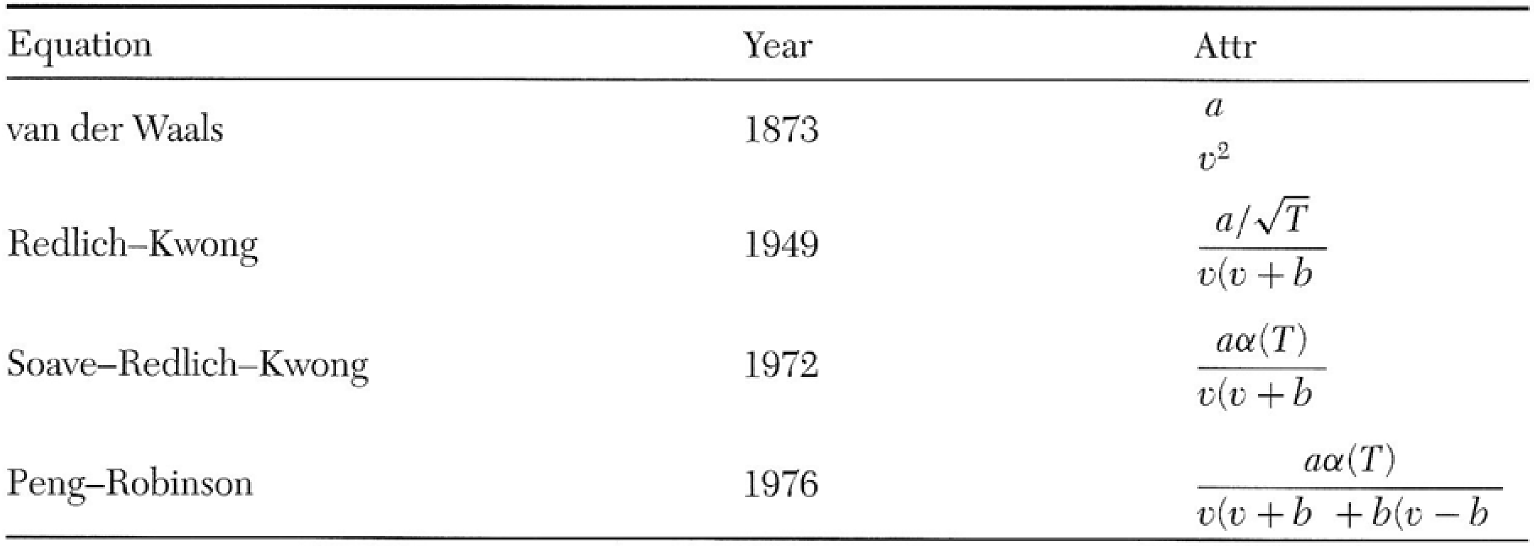


TABLE 4.3 Parameters for Some Popular Cubic Equations of State of the Form $P = RT/(v - b) - \text{Attr}$

Equation	Year	Attr
van der Waals	1873	$\frac{a}{v^2}$
Redlich–Kwong	1949	$\frac{a/\sqrt{T}}{v(v+b}$
Soave–Redlich–Kwong	1972	$\frac{a\alpha(T)}{v(v+b}$
Peng–Robinson	1976	$\frac{a\alpha(T)}{v(v+b\ +b(v-b}$

Cubic Equations of State

- **Redlich-Kwong EOS**

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)}$$

$$a = \frac{0.42748 R^2 T_c^{2.5}}{P_c}$$

$$b = \frac{0.08664 R T_c}{P_c}$$

Z_c=0.33 instead of 0.29

- **Peng-Robinson EOS**

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

$$a = 0.45724 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.07780 \frac{R T_c}{P_c}$$

$$\alpha(T) = [1 + \kappa(1 - \sqrt{T_r}]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

Z_c=0.307

Cubic Equations of State

❖ *Virial EOS*

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \cdots$$

Second Virial coefficient

Third Virial coefficient

The Virial coefficients are f(T) only!

$$z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + D'P^3 + \cdots \Rightarrow \begin{cases} B' = \dfrac{B}{RT} \\ C' = \dfrac{C - B^2}{(RT)^2} \end{cases}$$

- ❖ At moderate pressures (up to **15 bar**) when you keep the second Virial coefficient the power series expansion in pressure is more accurate:

$$z = \frac{Pv}{RT} = 1 + B'P = 1 + \frac{BP}{RT}$$

- ❖ From **15-50 bar**, the Virial equation should have three terms in terms of density:

$$z = 1 + \frac{B}{v} + \frac{C}{v^2}$$

EOS for Liquids and Solids

- Liquid and solid molar volumes are straightforward to measure in the lab, since these volumes are much less sensitive to temperature and pressure than gases.
- The temperature and pressure dependencies of volume can be measured by:

1. Thermal expansion coefficient: $\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$
2. Isothermal compressibility: $k \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$

See Table 4.4

- The liquid volume at saturation, Rackett eq.:

$$\boxed{v^{\mathrm{l,sat}} = \frac{RT_c}{P_c}(0.29056 - 0.08775\omega)^{\left[1+(1-T_r)^{2/7}\right]}}$$

Generalized Compressibility Charts

- The principle of corresponding states invokes a unique generalized relation between the compressibility factor, z, P_r, and T_r for a given class of molecules.
- It is more convenient to represent these in graphs or tables i.e. Compressibility Charts. To account for different classes of molecules we use:

$$z = z^{(0)} + \omega z^{(1)}$$

accounts for simple molecules

accounts for the nonsphericity of the molecules

- Values of $z^{(0)}$ and $z^{(1)}$ vs. P_r at different values of T_r are shown in Figures 4.13 and 4.14. The same data are reported in Appendix C.

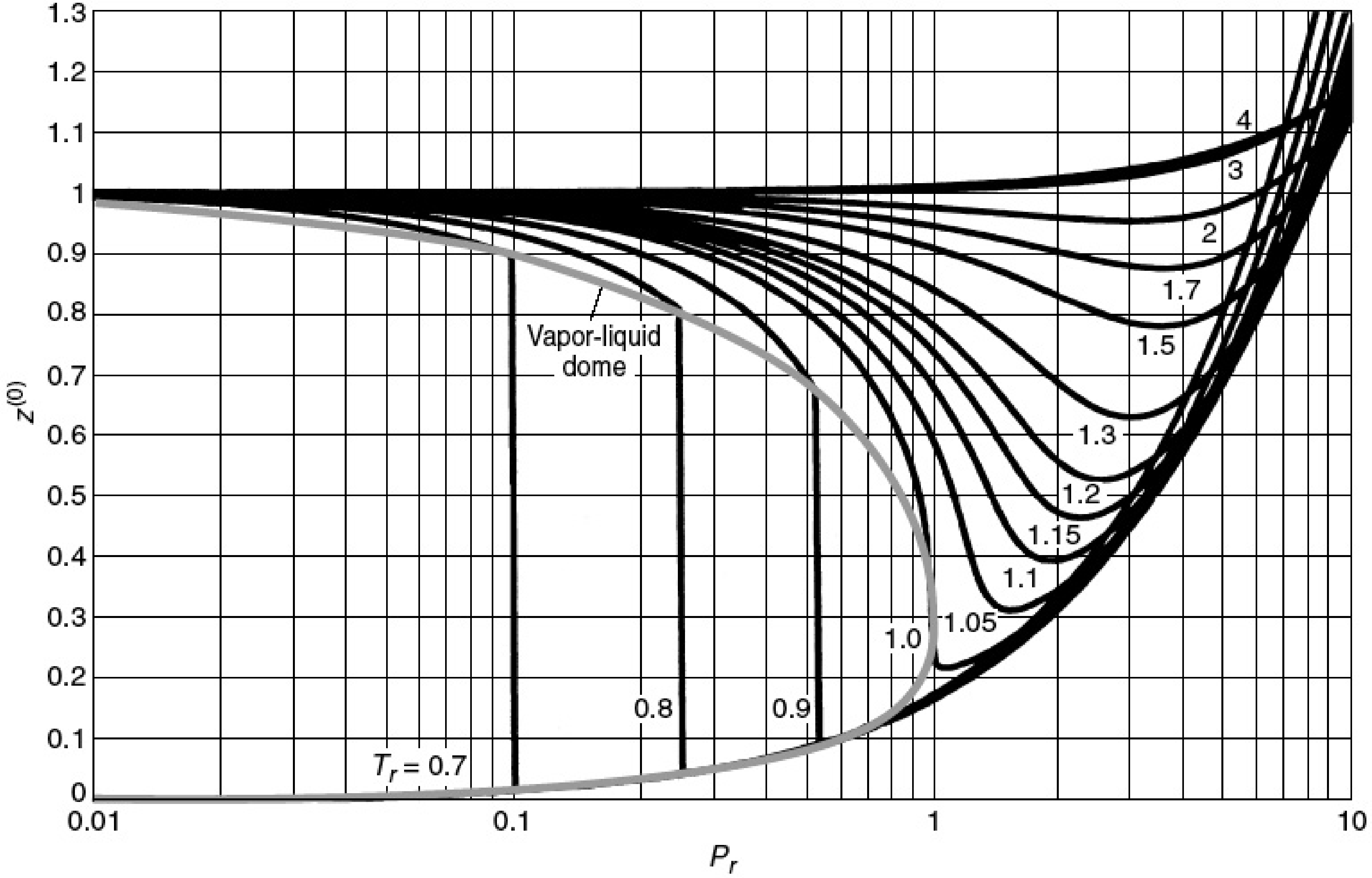


Figure 4.13 Generalized compressibility factor—simple fluid term. Based on the Lee–Kesler equation of state.

Example 4.9

Calculate the volume occupied by 10 kg of butane at 50 bar and 60°C using the Redlich–Kwong equation and the generalized compressibility charts.

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)} \Rightarrow \left\{ \begin{aligned} a &= \frac{0.42748R^2T_c^{2.5}}{P_c} = 29.08\left[\frac{\mathrm{JK^{1/2}m^3}}{\mathrm{mol^2}}\right] \\ b &= \frac{0.08664RT_c}{P_c} = 8.09 \times 10^{-5}\left[\frac{\mathrm{m^3}}{\mathrm{mol}}\right] \end{aligned} \right.$$

Solving by trial and error, we get: $v = 1.2 \times 10^{-4}\ [\mathrm{m^3/mol}] \Rightarrow \boxed{V = \frac{m}{MW} \times v = \frac{10}{.05812} \times 1.20 \times 10^{-4} = 0.021\ [\mathrm{m^3}]}$

Using the compressibility charts $\Rightarrow P_r = \frac{P}{P_c} = \frac{50\ \text{bar}}{38.9\ \text{bar}} = 1.32,\ \ T_r = \frac{T}{T_c} = \frac{333.2\ K}{345.2\ K} = 0.78,\ \ \text{and } \omega = 0.199$

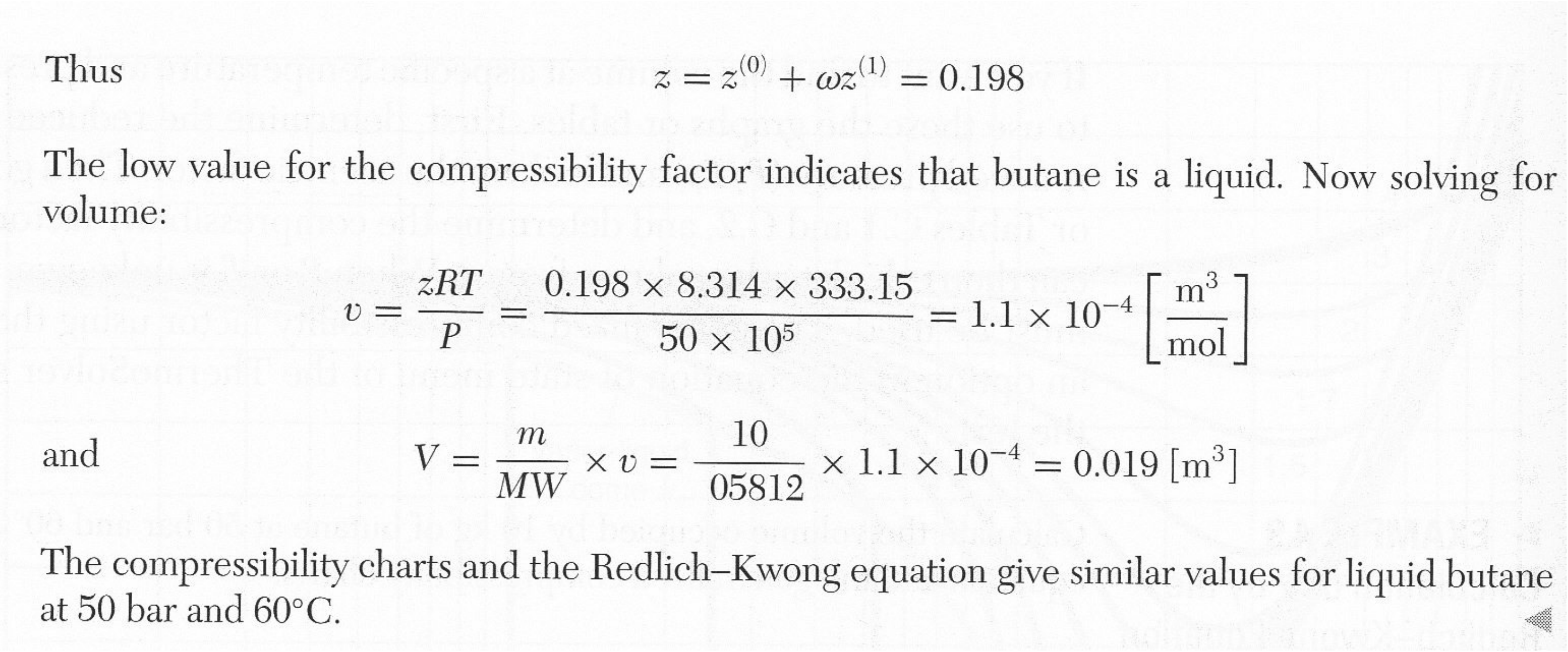
From Tables C.1 and C.2, we get:

	z^0			z^1	
	P_r			P_r	
T_r	1.3	1.4	T_r	1.3	1.4
0.75	0.2142	0.2303	0.75	−0.0871	−0.0934
0.78 (interpolated)	**0.2116**	**0.2274**		**−0.0843**	**−0.0903**
0.80	0.2099	0.2255	0.80	−0.0825	−0.0883

Example 4.9, Continue…

$$z^{(0)} = 0.2116 + \frac{0.02}{0.1}(0.2274 \quad 0.2116) = 0.2148$$

$$z^{(1)} = -0.0843 + \frac{0.02}{0.1}(-0.0903 \quad -0.0843)) = -0.0855$$



Thus $$z = z^{(0)} + \omega z^{(1)} = 0.198$$

The low value for the compressibility factor indicates that butane is a liquid. Now solving for volume:

$$v = \frac{zRT}{P} = \frac{0.198 \times 8.314 \times 333.15}{50 \times 10^5} = 1.1 \times 10^{-4} \left[\frac{\text{m}^3}{\text{mol}}\right]$$

and $$V = \frac{m}{MW} \times v = \frac{10}{05812} \times 1.1 \times 10^{-4} = 0.019\ [\text{m}^3]$$

The compressibility charts and the Redlich–Kwong equation give similar values for liquid butane at 50 bar and 60°C.

Determination of Parameters for Mixtures

- In chemical processes we are usually concerned with mixtures. The objective is to use properties of the pure substances then infer the properties of the mixture by using mixing rules.

- **Van der Waals:**

$$\boxed{a_{\text{mix}} = y_1^2 a_1 + 2y_1y_2a_{12} + y_2^2 a_2} \qquad \boxed{b_{\text{mix}} = y_1 b_1 + y_2 b_2}$$

$$\begin{cases} a_{12} = \sqrt{a_1 a_2} & \text{: Cross Coefficient} \\ a_{12} = \sqrt{a_1 a_2}(1 - k_{12}) \end{cases}$$

binary interaction parameter

- **Multicomponent Mixture:**

$$\boxed{a_{\text{mix}} = \sum_i \sum_j y_i y_j a_{ij}} \qquad \boxed{b_{\text{mix}} = \sum_i y_i b_i}$$

Determination of Parameters for Mixtures

- **Soave-Redlich-Kwong and Peng-Robinson:**

$$\boxed{a_{\mathrm{mix}} = \sum_i \sum_j y_i y_j [a\alpha(T)]_{ij}} \qquad \boxed{b_{\mathrm{mix}} = y_1 b_1 + y_2 b_2}$$

Corresponding States in Mixtures

- We need to find P_c, T_c, ω_c for the mixture, Kay's rule:

$$T_{pc} = \sum y_i T_{c,i} \qquad P_{pc} = \sum y_i T_{c,i} \qquad \omega_{pc} = \sum y_i \omega_{c,i}$$

$$T_{pc,ij} = \sqrt{T_{c,i} T_{c,j}} \qquad T_{pc,ij} = \sqrt{T_{c,i} T_{c,j}}(1 - k'_{ij})$$

General Strategy

1. Check whether conditions represent ideal gas.
   - If they do then use *pv=RT*
   - *If they do not then:*

2. Use an approach which includes non-idealities
   - If ***P*** and ***T*** are given: Use the *compressibility* charts directly.
   - If ***T*** and ***v*** are given: Use *Redlich-Kwong* equation:

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)} \Longrightarrow \begin{cases} a = \dfrac{0.42748R^2T_c^{\,2.5}}{P_c} \\ b = \dfrac{0.08664RT_c}{P_c} \end{cases}$$

Example 4.10

Calculate the following:

(a) The volume occupied by 20 kg of propane at 100°C and 70 bar
(b) The pressure needed to fill a 0.1 m^3-vessel at room temperature to store 50 mol of propane
(c) The pressure needed to fill a 0.1 m^3-vessel at room temperature to store a mixture of 20 mol of propane and 30 mol of ethane

(a) At 70 bar, propane is not an ideal gas. Since we are given T and P we can use the compressibility charts directly. First, we need to find the reduced pressure and reduced temperature using the critical data available in Appendix A:

$$P_r = \frac{P}{P_c} = \frac{70\text{ bar}}{42.4\text{ bar}} = 1.65 \quad \text{and} \quad T_r = \frac{T}{T_c} = \frac{373\ K}{370\ K} = 1.01$$

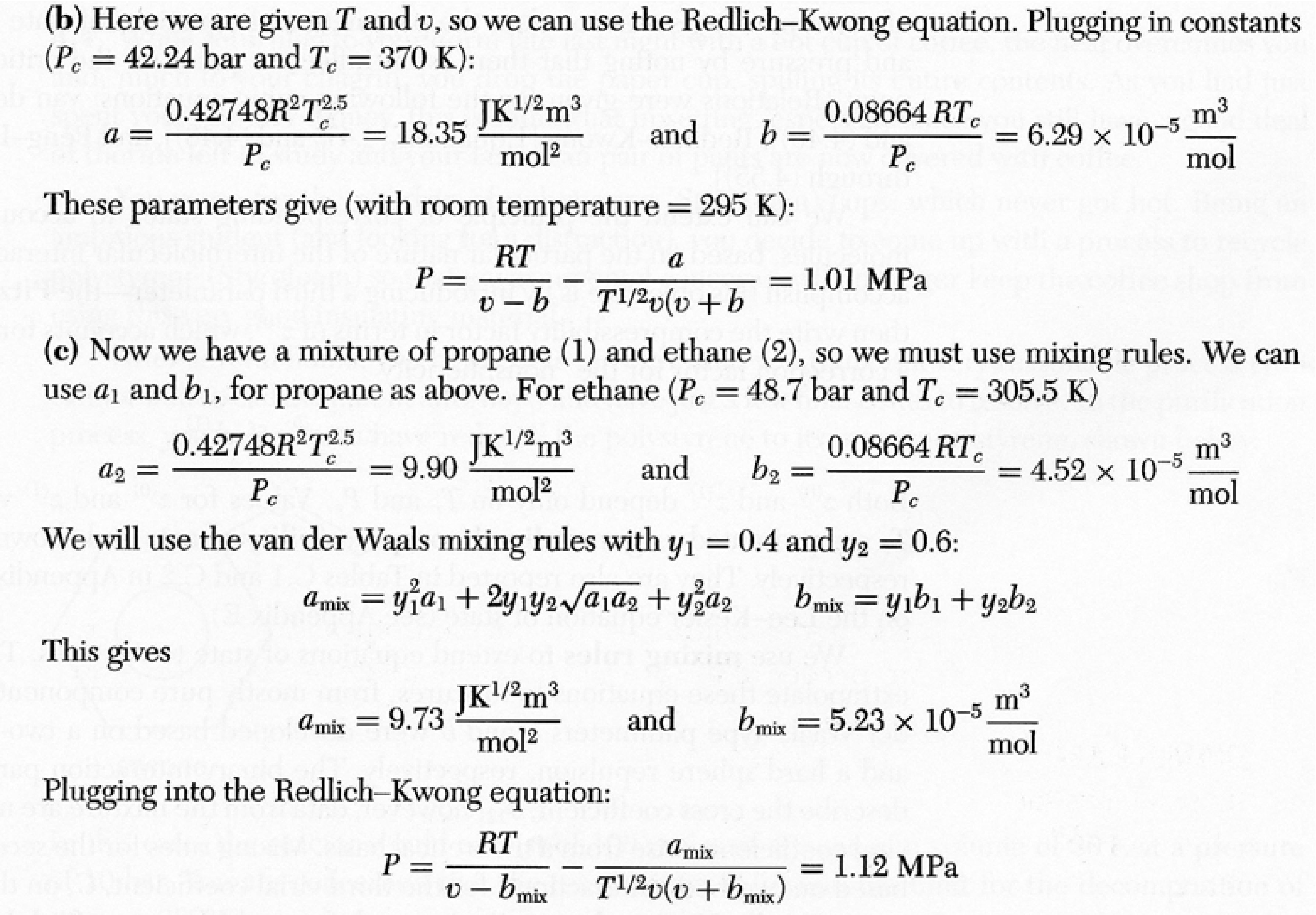
We also have to look up the value of the acentric factor·

$$\omega = 0.153$$

Interpolating from Tables C.1 and C.2,

$$z = z^{(0)} + \omega z^{(1)} = 0.2822 + 0.153 \times \ -0.0670) = 0.272$$

So $$V = nv = \frac{m}{MW}\left(\frac{zRT}{P}\right) = \frac{20 \times 10^3}{44}\left(\frac{0.272 \times 8.314 \times 373}{70 \times 10^5}\right) = 0.0548\text{ m}^3$$



(b) Here we are given T and v, so we can use the Redlich–Kwong equation. Plugging in constants ($P_c = 42.24$ bar and $T_c = 370$ K):

$$a = \frac{0.42748 R^2 T_c^{2.5}}{P_c} = 18.35\ \frac{\text{JK}^{1/2}\text{m}^3}{\text{mol}^2} \quad \text{and} \quad b = \frac{0.08664\, RT_c}{P_c} = 6.29 \times 10^{-5}\ \frac{\text{m}^3}{\text{mol}}$$

These parameters give (with room temperature = 295 K):

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b} = 1.01 \text{ MPa}$$

(c) Now we have a mixture of propane (1) and ethane (2), so we must use mixing rules. We can use a_1 and b_1, for propane as above. For ethane ($P_c = 48.7$ bar and $T_c = 305.5$ K)

$$a_2 = \frac{0.42748 R^2 T_c^{2.5}}{P_c} = 9.90\ \frac{\text{JK}^{1/2}\text{m}^3}{\text{mol}^2} \qquad \text{and} \qquad b_2 = \frac{0.08664\, RT_c}{P_c} = 4.52 \times 10^{-5}\ \frac{\text{m}^3}{\text{mol}}$$

We will use the van der Waals mixing rules with $y_1 = 0.4$ and $y_2 = 0.6$:

$$a_{\text{mix}} = y_1^2 a_1 + 2y_1 y_2 \sqrt{a_1 a_2} + y_2^2 a_2 \qquad b_{\text{mix}} = y_1 b_1 + y_2 b_2$$

This gives

$$a_{\text{mix}} = 9.73\ \frac{\text{JK}^{1/2}\text{m}^3}{\text{mol}^2} \qquad \text{and} \qquad b_{\text{mix}} = 5.23 \times 10^{-5}\ \frac{\text{m}^3}{\text{mol}}$$

Plugging into the Redlich–Kwong equation:

$$P = \frac{RT}{v - b_{\text{mix}}} - \frac{a_{\text{mix}}}{T^{1/2} v (v + b_{\text{mix}})} = 1.12 \text{ MPa}$$