0905322- Chemical Engineering Thermodynamics I
Lecture 6: Equations of State

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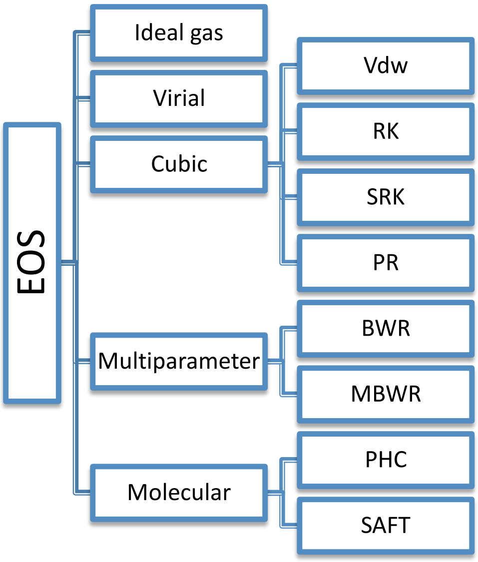
Outline

- ○Volumetric Equations of State
- ○Ideal Gas (IG) EOS
- ○Virial EOS
- ○Generalized Compressibility Factor Chart
- ○Corresponding States Principle (CSP)
- ○Cubic EOS
- ○BWR and MBWR

Volumetric Equations of State

- A mathematical formula that relates the pressure (*P*), temperature (*T*), and specific volume (*v*) of a substance is called an equation of state (EOS).

$$f(P, v, T) = 0$$
$$v = v(T, P)$$



- EOS
  - Ideal gas
  - Virial
  - Cubic
    - Vdw
    - RK
    - SRK
    - PR
  - Multiparameter
    - BWR
    - MBWR
  - Molecular
    - PHC
    - SAFT

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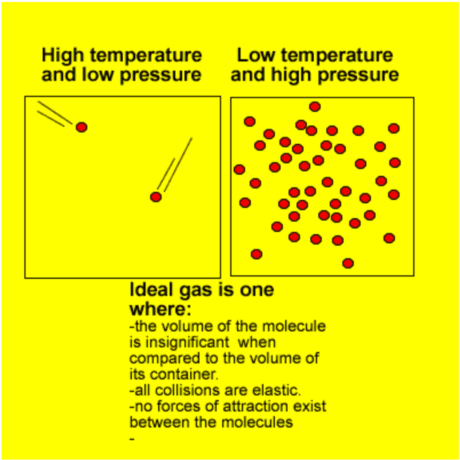
Ideal Gas (IG) EOS

- The easiest yet the least accurate.
- Applies to gas phase only.
- Two main assumptions:
  - Molecular size is zero!
  - No molecular forces.

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

- Parameter is R called universal gas constant with a value of 8.314 J/mol.K.



Ideal gas is one where:
-the volume of the molecule is insignificant when compared to the volume of its container.
-all collisions are elastic.
-no forces of attraction exist between the molecules
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Virial EOS

- A series expansion around the IG limit.
  - Pressure form

$$Z = 1 + B'P + C'P^2 + \cdots$$

  - Volume form

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots$$

$$B' = \frac{B}{RT}$$

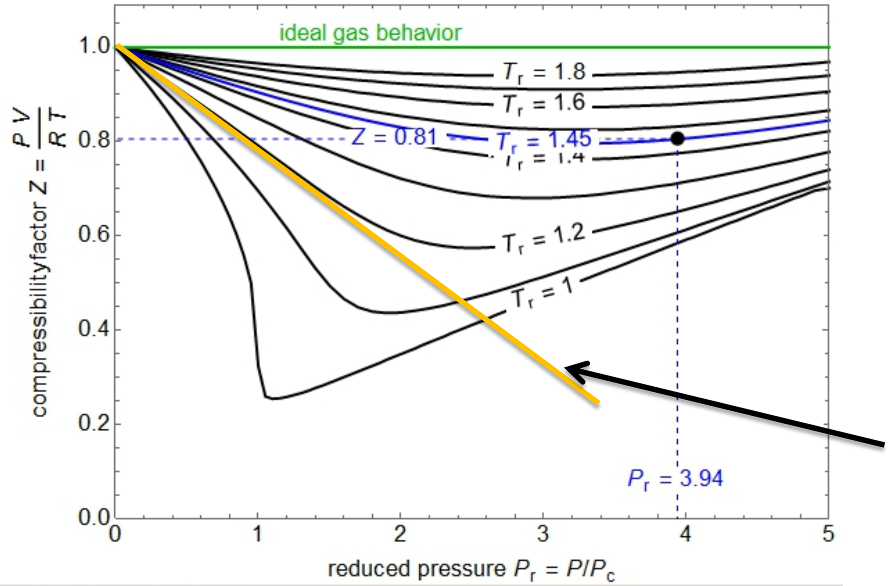
- More accurate than the IG EOS.
- Applies to gas phase only.

Virial Coefficients

The virial coefficients are function of temperature only. They are related to molecular forces from statistical mechanics

B is related to two body interactions. C is related to three body interactions and so on.

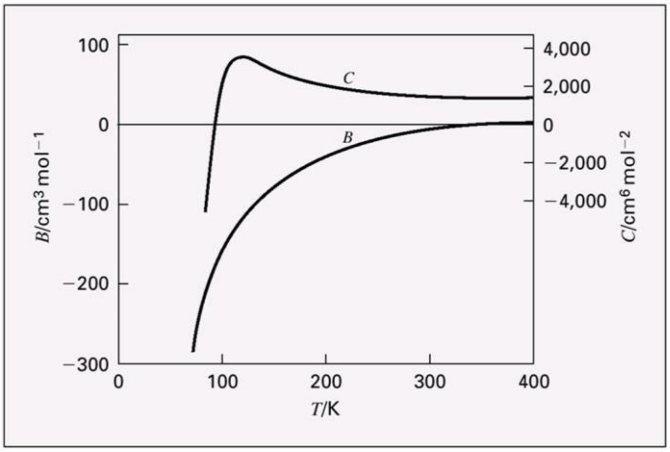
IG applicability limits Z =1
High temperature and Low pressure



$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$$

$$\lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = \frac{B}{RT} = B'$$

Effect of T on Virial Coefficients



Second and third virial coefficients for nitrogen (Fig. 3-10 in Smith and van Ness)

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

Pitzer's Correlation for the Second Virial Coefficient

- Applies to nonpolar gases

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

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

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}, \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

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

$$Z^0 = 1 + B^0\frac{P_r}{T_r}, \qquad Z^1 = B^1\frac{P_r}{T_r}$$

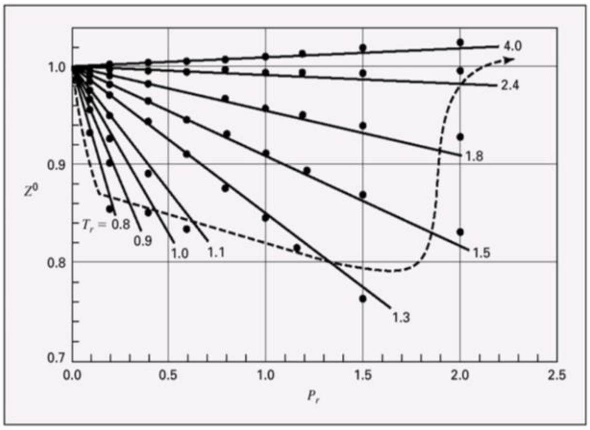


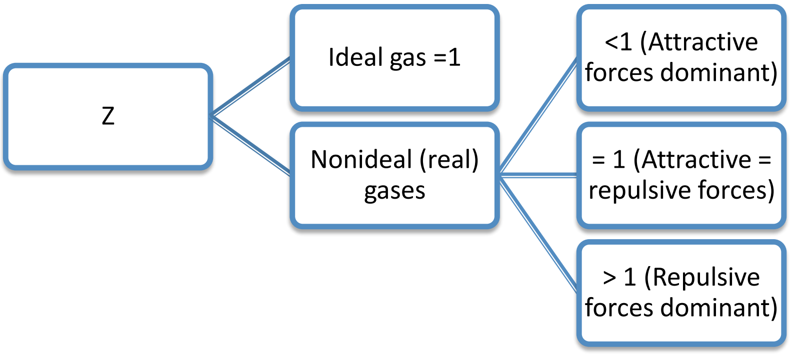
Figure 3.14: Comparison of correlations for Z^0. The virial-coefficient correlation is represented by the straight lines; the Lee/Kesler correlation, by the points. In the region above the dashed line the two correlations differ by less than 2%.

Generalized Compressibility Factor Chart

- The compressibility factor Z can be thought of as the ratio of the volume of the nonideal (real) gas to that of an ideal gas at the same conditions.

$$Z = \frac{Pv}{RT} = \frac{v_{\text{nonideal}}}{v_{\text{Ideal gas}}}$$

$$Pv = ZRT$$



Corresponding States Principle (CSP)

- The Z factor for all gases is approximately the same at the same reduced pressure (P_r) and temperature (T_r).

$$Z = Z(T_r, P_r)$$

  - This is the two parameter CSP.
  - The chart is for the majority of hydrocarbon gases with $Z_c \sim 0.27$.

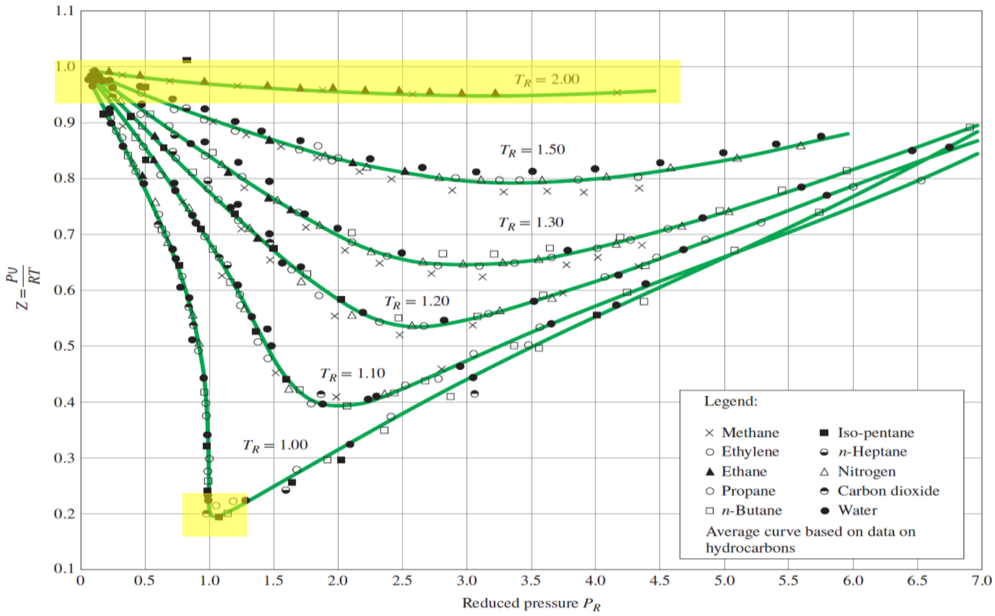


FIGURE 3–48

Comparison of Z factors for various gases.

Source: Gour-Jen Su, "Modified Law of Corresponding States," *Ind. Eng. Chem.* (international ed.) 38 (1946), p. 803.

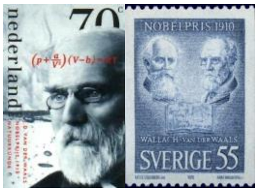
Van der Waal's (vdW) EOS

- Developed in 1873.
- vdW relaxed the assumptions of the ideal gas:
  - Molecules do have a volume.
  - Molecules do have intermolecular forces that are manifested as a pressure exerted on the container wall.
- The first EOS to apply for both the vapor and liquid phases.

Attractive

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

Repulsive



vdW EOS Parameters

- The vdW EOS has two parameters
  - A volume correction called **covolume** (*b*).
  - A pressure correction called **energy parameter** (*a*)
- Substance specific.
- Obtained from the conditions at the critical point.

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0$$

$$a = \frac{27}{64}\frac{\left(RT_c\right)^2}{P_c}, \quad b = \frac{1}{8}\frac{\left(RT_c\right)}{P_c}$$

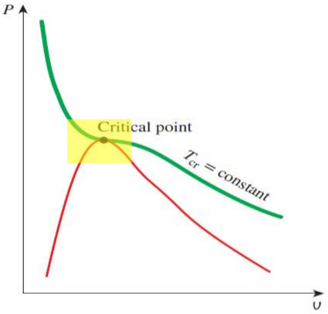


FIGURE 3–55
Critical isotherm of a pure substance has an inflection point at the critical state.

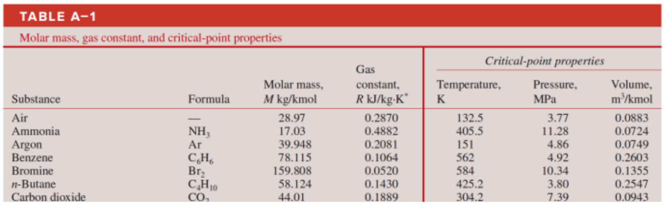


TABLE A–1

Molar mass, gas constant, and critical-point properties

Substance	Formula	Molar mass, *M* kg/kmol	Gas constant, *R* kJ/kg·K*	Critical-point properties: Temperature, K	Pressure, MPa	Volume, m³/kmol
Air	—	28.97	0.2870	132.5	3.77	0.0883
Ammonia	NH_3	17.03	0.4882	405.5	11.28	0.0724
Argon	Ar	39.948	0.2081	151	4.86	0.0749
Benzene	C_6H_6	78.115	0.1064	562	4.92	0.2603
Bromine	Br_2	159.808	0.0520	584	10.34	0.1355
n-Butane	C_4H_{10}	58.124	0.1430	425.2	3.80	0.2547
Carbon dioxide	CO_2	44.01	0.1889	304.2	7.39	0.0943

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Cubic EOS

- vdW is the first cubic EOS (in volume or compressibility factor) successful in qualitatively describing both vapor and liquid phases.
- Yet, it is not accurate.
- Various modifications
  - 1949 Redlick-Kwong (RK) EOS: energy parameter, *a*, is function of T.
  - 1972 Soave-RK (SRK)
  - 1976 Peng-Robinson (PR)

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Cubic EOS

Redlich-Kwong (RK)

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

$$a = 0.42748\frac{(RT_c)^2\sqrt{T_c}}{P_c}$$

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

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

$$Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$$

	vdW	SRK	PR
α	$-1 - B$	-1	$-1 + B$
β	A	$A - B - B^2$	$A - 2B - 3B^2$
γ	$-AB$	$-AB$	$-AB + B^2 + B^3$
Z_c	0.3750	0.3333	0.3074

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

Initial Guess for solution

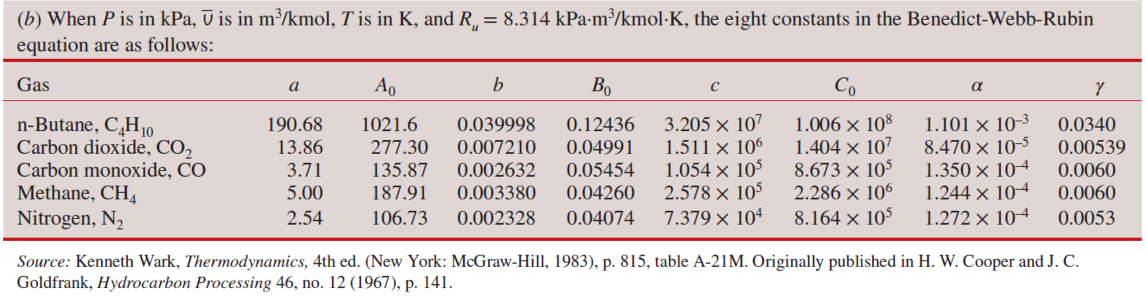
Vapor (Vapor like): ideal gas ($Z = 1$).

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

Benedict-Webb-Rubin (BWR) EOS

- Original BWR

$$P=\frac{RT}{v}+\left(B_0RT-A_0-\frac{C_0}{T^2}\right)\frac{1}{v^2}+\frac{bRT-a}{v^3}+\frac{a\alpha}{v^6}+\frac{c}{v^3T^2}\left(1+\frac{\gamma}{v^2}\right)e^{-\frac{\gamma}{v^2}}$$



(*b*) When P is in kPa, $\bar{v}$ is in m^3/kmol, T is in K, and $R_u = 8.314$ kPa·m^3/kmol·K, the eight constants in the Benedict-Webb-Rubin equation are as follows:

Gas	a	A_0	b	B_0	c	C_0	α	γ
n-Butane, C_4H_{10}	190.68	1021.6	0.039998	0.12436	3.205×10^7	1.006×10^8	1.101×10^{-3}	0.0340
Carbon dioxide, CO_2	13.86	277.30	0.007210	0.04991	1.511×10^6	1.404×10^7	8.470×10^{-5}	0.00539
Carbon monoxide, CO	3.71	135.87	0.002632	0.05454	1.054×10^5	8.673×10^5	1.350×10^{-4}	0.0060
Methane, CH_4	5.00	187.91	0.003380	0.04260	2.578×10^5	2.286×10^6	1.244×10^{-4}	0.0060
Nitrogen, N_2	2.54	106.73	0.002328	0.04074	7.379×10^4	8.164×10^5	1.272×10^{-4}	0.0053

Source: Kenneth Wark, *Thermodynamics,* 4th ed. (New York: McGraw-Hill, 1983), p. 815, table A-21M. Originally published in H. W. Cooper and J. C. Goldfrank, *Hydrocarbon Processing* 46, no. 12 (1967), p. 141.

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Modified Benedict-Webb-Rubin (MBWR) EOS

- Modified BWR (MBWR)

$$P=\sum_{n=1}^{9}\frac{a_n}{v^n}+e^{-\frac{\gamma}{v^2}}\sum_{n=10}^{17}\frac{a_n}{v^{2n-17}},\quad \gamma=1/\rho_c^2$$

$$P=\sum_{n=1}^{9}a_n\rho^n+e^{-\gamma\rho^2}\sum_{n=10}^{17}a_n\rho^{2n-17}$$

Download the student version of NIST's **refprops** software and check the pure component options available.

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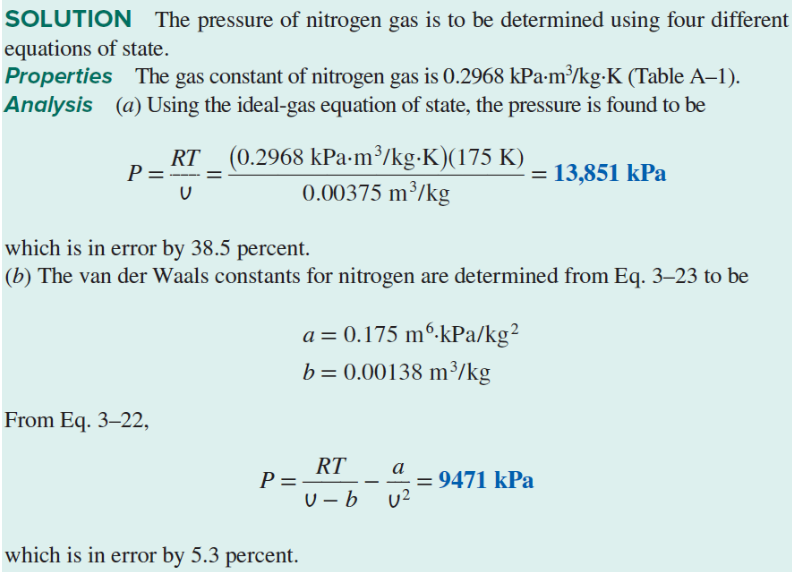
EXAMPLE 3–13 Different Methods of Evaluating Gas Pressure

Predict the pressure of nitrogen gas at T = 175 K and v = 0.00375 $\mathrm{m_3}$/kg on the basis of (*a*) the ideal-gas equation of state, (*b*) the van der Waals equation of state, (*c*) the Beattie-Bridgeman equation of state, and (*d*) the Benedict-Webb-Rubin equation of state. Compare the values obtained to the experimentally determined value of 10,000 kPa.



SOLUTION The pressure of nitrogen gas is to be determined using four different equations of state.

Properties The gas constant of nitrogen gas is 0.2968 kPa·m^3/kg·K (Table A–1).

Analysis (*a*) Using the ideal-gas equation of state, the pressure is found to be

$$P = \frac{RT}{v} = \frac{(0.2968\ \text{kPa·m}^3/\text{kg·K})(175\ \text{K})}{0.00375\ \text{m}^3/\text{kg}} = \mathbf{13{,}851\ kPa}$$

which is in error by 38.5 percent.

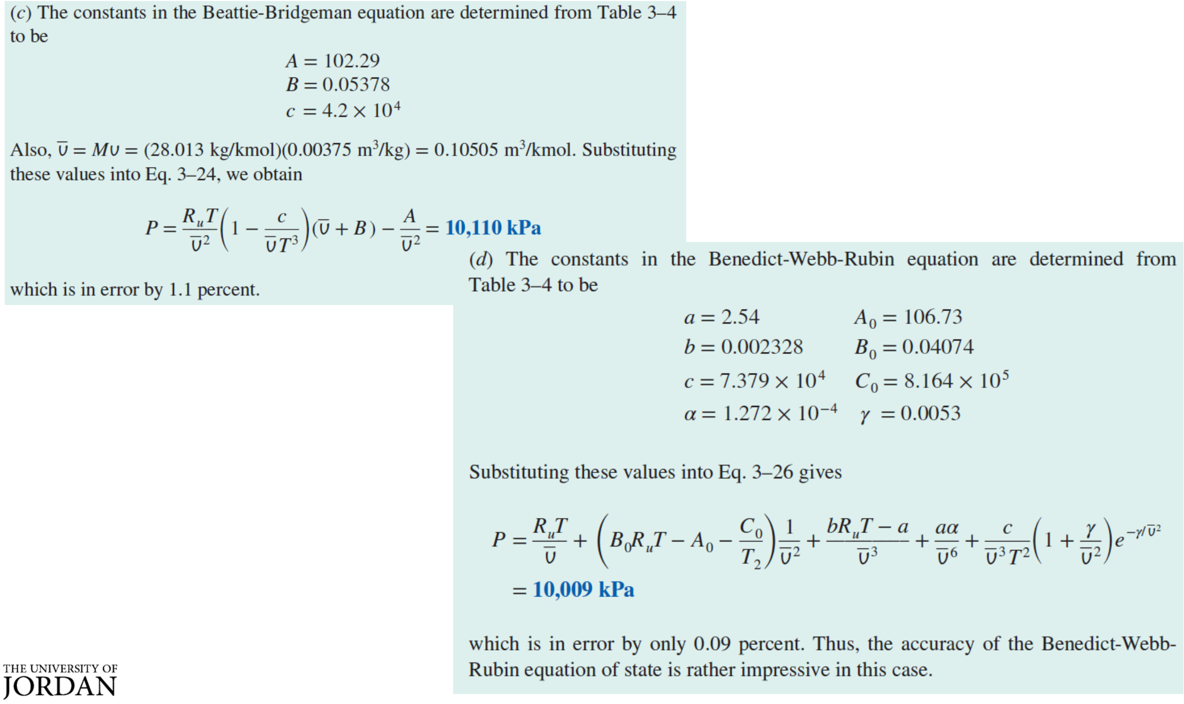
(*b*) The van der Waals constants for nitrogen are determined from Eq. 3–23 to be

$$a = 0.175\ \text{m}^6\text{·kPa/kg}^2$$
$$b = 0.00138\ \text{m}^3/\text{kg}$$

From Eq. 3–22,

$$P = \frac{RT}{v - b} - \frac{a}{v^2} = \mathbf{9471\ kPa}$$

which is in error by 5.3 percent.



(*c*) The constants in the Beattie-Bridgeman equation are determined from Table 3–4 to be

$$A = 102.29$$
$$B = 0.05378$$
$$c = 4.2 \times 10^4$$

Also, $\bar{v} = Mv$ = (28.013 kg/kmol)(0.00375 m^3/kg) = 0.10505 m^3/kmol. Substituting these values into Eq. 3–24, we obtain

$$P = \frac{R_u T}{\bar{v}^2}\left(1 - \frac{c}{\bar{v}T^3}\right)(\bar{v} + B) - \frac{A}{\bar{v}^2} = \mathbf{10{,}110\ kPa}$$

which is in error by 1.1 percent.

(*d*) The constants in the Benedict-Webb-Rubin equation are determined from Table 3–4 to be

$a = 2.54$ $\quad A_0 = 106.73$
$b = 0.002328$ $\quad B_0 = 0.04074$
$c = 7.379 \times 10^4$ $\quad C_0 = 8.164 \times 10^5$
$\alpha = 1.272 \times 10^{-4}$ $\quad \gamma = 0.0053$

Substituting these values into Eq. 3–26 gives

$$P = \frac{R_u T}{\bar{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T_2}\right)\frac{1}{\bar{v}^2} + \frac{bR_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2}\left(1 + \frac{\gamma}{\bar{v}^2}\right)e^{-\gamma/\bar{v}^2}$$
$$= \mathbf{10{,}009\ kPa}$$

which is in error by only 0.09 percent. Thus, the accuracy of the Benedict-Webb-Rubin equation of state is rather impressive in this case.