Solutions Manual for
Fundamentals of Chemical Engineering Thermodynamics

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Note to the Instructor
An effort was made to update all solutions requiring steam tables to conform with the tables in Appendix E of the book, which are based on IAPWS95). It is possible, however, that some problems may make use of older tables. Be alert as such discrepancies could confuse students even though the final answers are not much different.

Please report any mistakes or typos to Themis Matsoukas: matsoukas@psu.edu.

Contents

1 Introduction

Problem 1.1 Solution

We will need the following unit conversions:

$$1 \text{ ft} = 0.3048 \text{ m}, \qquad 1 \text{ lb} = 0.454 \text{ kg}, \qquad 1 \text{ lbmol} = 454 \text{ mol}$$

(Note on the conversion mol to lbmol: one mol has a mass equal to the molecular weight in g, while one lbmol has a mass equal equal to the molecular weight in lb.) We also need the molar mass of ammonia which is

$$M_m = 17 \text{ g/mol} = 17 \times 10^{-3} \text{ kg/mol}$$

a) Specific Volume:

$$V = \frac{1}{41.3 \text{ lb/ft}^3} = 0.02421 \text{ ft}^3/\text{lb} = 0.00151 \text{ m}^3/\text{kg} = 1.51 \text{ cm}^3/\text{g}$$

b) Molar Volume

$$V_{\text{molar}} = VM_m = 2.567 \times 10^{-5} \text{ m}^3/\text{mol} = 25.67 \text{ cm}^3/\text{mol} = 0.4116 \text{ ft}^3/\text{lb-mol}$$

Problem 1.2 Solution First we write the given equation as

$$T_K = \frac{B}{A - (\ln P_{\text{bar}})/(\ln 10)} - C$$

where T_K refers to T in kelvin, P_{bar} refers to pressure in bar, and the logarithm is natural. Next we use

$$T_F = 1.8(T_K - 273.15) + 32 \quad \text{and} \quad P_{\text{bar}} = \frac{P_{\text{psi}}}{14.5}$$

and substitute these values into the above equation. After some manipulation the result is

$$T_F = \frac{B(1.8)(\ln 10)}{A \ln 10 + \ln(14.5) - \ln P_{\text{psi}}} - C(1.8) - (1.8)(273.15) + 32$$

Doing the algebra,

$$T_F = \frac{5062.37}{13.2153 - \ln P_{\text{psi}}} - 302.217$$

Therefore,

$$A' = 13.2153, \quad B' = 5062.37 \quad C' = 302.217$$

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Problem 1.3 Solution a) The mean velocity is

$$\bar{v} = \left(\frac{8 k_B T}{\pi m} \right)^{1/2}$$

where $k_B = 1.38 \times 10^{-23}$ J/K, $T = 273.16$ K. The mass of the water molecule is

$$m = \frac{M_m}{N_{AV}} = \frac{18 \times 10^{-3} \text{ kg/mol}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.98904 \times 10^{-26} \text{ kg.}$$

The mean velocity is

$$\bar{v} = 566.699 \text{ m/s} = 2040.12 \text{ km/h} = 1267 \text{ mph}$$

This result depends only on temperature and since all three phases are the same temperature, molecules have the same mean velocity in all three phases.

b) The mean kinetic energy is

$$\bar{E}_{\text{kin}} = \overline{\tfrac{1}{2} m v^2} = \tfrac{1}{2} m \overline{v^2}$$

where $\overline{v^2}$ is the mean squared velocity,

$$\overline{v^2} = \frac{3 k_B T}{m}.$$

With this the mean kinetic energy is

$$\bar{E}_{\text{kin}} = \frac{3}{2} k_B T = 5.65441 \times 10^{-21} \text{ J}$$

This is the mean kinetic energy per molecule in all phases. The number of molecules in 1 kg of water is

$$N = \frac{1 \text{ kg}}{18 \times 10^{-3} \text{ kg/mol}} 6/022 \times 10^{23} = 3.34556 \times 10^{25}$$

The total kinetic energy in 1 kg of water at 0.01 °C (regardless of phase) is

$$\bar{E}_{\text{kin}} = \left(5.65441 \times 10^{-21} \text{ J} \right) \left(3.34556 \times 10^{25} \right) = 189,171 \text{ J} = 189 \text{ kJ}$$

Comment: This is the *translational* kinetic energy of the molecule, i.e., the kinetic energy due to the motion of the center of mass. A water molecule possesses additional forms of kinetic energy that arise from the rotation of the molecule, the bending of bonds, and the vibration of oxygen and hydrogen atoms about their equilibrium positions. These are not included in this calculation as the Maxwell-Boltzmann distribution refers specifically to the translational kinetic energy.

c) The above calculation shows that the mean kinetic energy depends *only on temperature* (it is independent of pressure or of the mass of the molecule). Therefore, oxygen at 0.01 °C has the same kinetic energy as water at the same temperature:

$$\bar{E}_{\text{kin}} = \frac{3}{2} k_B T = 5.65441 \times 10^{-21} \text{ J}$$

Problem 1.4 Solution
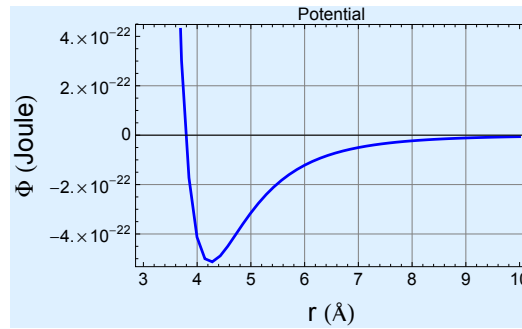
a) The potential has a minimum just above 4 Å or so. To determine this value accurately we must set the derivative of the potential equal to zero solve for the value of r. To do this easily, we define a new variable $x = r/\sigma$ and rewrite the potential as:

$$\Phi = a\left(x^{-12} - x^{-6}\right)$$

By chain rule we now have:

$$\frac{dF}{dr} = \frac{dF}{dx}\frac{dx}{dr} = \left(-12x^{-13} + 6x^{-7}\right)\frac{dx}{dr}$$

Setting this to zero and solving for x we have:

$$-12x^{-13} + 6x^{-7} = 0 \quad \Rightarrow \quad x = 2^{1/6}$$

Since $r = \sigma x$, the value of r that minimizes the potential is

$$r_* = 2^{1/6}\sigma = (4.24964)(3.786\ \text{Å}) = 4.25\ \text{Å}$$

b) If we imagine N molecules to be situated at the center of cubes whose sides are equal to r_*,
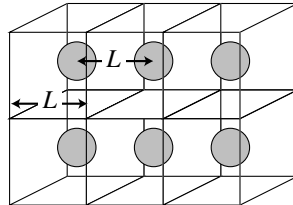
the volume occupied is

$$V = N(r_*)^3$$

These N molecules correspond to N/N_{Av} mol and their total mass is

$$M = \frac{N}{N_{AV}}M_m$$

where M_m is the molar mass of methane ($M_m = 16 \cdot 10^{-3}$ kg/mol). For the density, therefore, we obtain the following final formula:

$$\rho = \frac{M_m}{N_{AV}(r_*)^3}$$

By numerical substitution we finally obtain the density:

$$\rho = \frac{16 \cdot 10^{-3}\ \text{kg/mol}}{(6.024 \cdot 10^{23}\ \text{mol}^{-1})(4.25\ \text{Å})(10^{-10}\ \text{m/Å})} = 346\ \text{kg/m}^3 = 0.346\ \text{g/cm}^3$$

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c) Specific volumes of saturated liquid methane are listed in Perry's Handbook from which we can compute the densities. We notice (as we would have expected) that liquid volumes near the critical point ($T_c =$ 190.55 K) vary with pressure, from 162.3 kg/m^3 at the critical point to 454 kg/m^3 around 90 K. Our value corresponds to Perry's tabulation at about 160 K. Our calculation is approximate and does not incorporate the effect of pressure and temperature. Notice that if we pick a distance somewhat different from r_* the result will change quite a bit because if the third power to which this distance is raised. But the important conclusion is that the calculation placed the density right in the correct range between the lowest and highest values listed in the tables. This says that our molecular picture of the liquid, however idealized, is fairly close to reality.

Problem 1.5 Solution

Assuming molecules to be sitting at the center of a cubic lattice with spacing L, the volume occupied by N molecules is NL^3 and the density is

$$\rho = \frac{M_m}{N_{AV}L^3}$$

where M_m is the molar mass. Solving for the intermolecular distance,

$$L = \left(\frac{M_m}{N_{AV}\rho}\right)$$

a) For liquid water with $\rho = 1000 \text{ kg/m}^3$,

$$L = \left(\frac{18 \times 10^{-3} \text{ kg/mol}}{(6.022 \times 10^{23} \text{ mol}^{-1})(1000 \text{ kg/m}^3)}\right)^{1/3} = 3.10 \times 10^{-10} \text{ m} = 3.01 \text{ Å}$$

b) For steam with $\rho = 0.4 \text{ kg/m}^3$

$$L = \left(\frac{18 \times 10^{-3} \text{ kg/mol}}{(6.022 \times 10^{23} \text{ mol}^{-1})(0.4 \text{ kg/m}^3)}\right)^{1/3} = 4.2 \times 10^{-9} \text{ m} = 42 \text{ Å}$$

The intermolecular distance is about 10 times larger in the vapor.

Problem 1.6 Solution
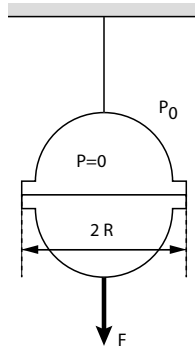
The force needed to separate the two haves is equal to the force that is exerted by pressure on one hemisphere:

$$F = \Delta P \; A$$

where ΔP is the pressure difference between the atmospheric pressure and the contents of the sphere, and A is the cross-sectional area of the sphere (πR^2). Assuming the sphere to be fully evacuated, the pressure difference is equal to the atmospheric pressure (≈ 1 bar $= 10^5$ Pa). The force now is

$$F = P_0(\pi R^2) = (10^5 \text{ Pa})(\pi 0.5^2 \text{ m}^2) = 19,635 \text{ N}$$

This force corresponds to a mass

$$M = \frac{F}{g} = \frac{39269.9 \text{ N}}{9.81 \text{ N/kg}} = 2,000 \text{ kg}.$$

Assuming an average weight of 80 kg/person, it would take the weight of 25 people (!) to separate the spheres.

2 Phase Diagrams of Pure Fluids

Problem 2.1 Solution a) 25 °C, 1 bar: liquid, because the temperature is below the saturation temperature at 1 bar (99.63°C).

10 bar, 80°C: liquid, because the temperature is below the saturation temperature at 10 bar (179.88 °C).

120 °C, 50 bar: At 120 °C the vapor pressure is 198.54 kPa = 1.9884 bar. Since the actual pressure is higher, the state is liquid. (*Or*, at 50 bar the saturation temperature is 263.91 °C. Since the actual temperature is lower the state is liquid.)

b) Liquid, because the pressure (1 atm = 760 mm Hg) is higher than the vapor pressure of bromobenzene (10 mg H) at the same temperature.

c) Liquid, because the temperature is lower than the boiling point at the same pressure.

Note: All of these statements will make better sense if you plot your information on the PV graph.

Problem 2.2 Solution a) From steam tables at 40 bar we collect the following data:

	600 °C	650 °C
40 bar	0.0989 m^3/kg	0.1049 m^3/kg

By interpolation at $V = 100$ g/cm^3 = 0.1 m^3/kg we find

$$T = 600 + \frac{650 - 600}{0.1049 - 0.0989}(0.1 - 0.0989) = 609.2\,°\text{C}$$

The system is at 40 bar, 609.2 °C: the phase is vapor.

b) At 6 bar we find that the desired volume lies between that of the saturated liquid ($V_L = 0.0011$ m^3/kg) and saturated vapor ($V_V = 0.3156$): the system is a vapor/liquid mixture. The vapor and liquid fractions are obtained by lever rule:

$$x_L = \frac{0.3156 - 0.1}{0.3156 - 0.0011} = 0.314 = 31.4\%$$
$$x_V = 1 - 0.314 = 0.686 = 68.6\%$$

Problem 2.3 Solution a) At 1 bar, 210 °C, the specific volume of steam is found by interpolation to be

$$V = 2219.2 \text{ cm}^3/\text{g} = 2.2192 \text{ m}^3/\text{kg}$$

Since the total volume of the vessel is 3.5 m³, the mass is

$$M = \frac{V^t}{V} = \frac{3.5 \text{ m}^3}{2.2192 \text{ m}^3/\text{kg}} = 1.577 \text{ kg}$$

b) Since the system is a mixture of liquid and vapor, it is saturated. From the saturated tables at 20 bar we find by interpolation the following:

$$T = 212.37 \text{ °C}, \quad V_L = 1.18 \text{ cm}^3/\text{g}, \quad V_V = 99.54 \text{ cm}^3/\text{g}$$

The specific volume of the mixture is

$$V = l V_L + v V_V = (0.85)(1.18) + (0.15)(99.54) = 15.93 \text{ cm}^3/\text{g}$$

The total volume required for storage is $V^t = MV$, where V is the specific volume calculated above:

$$V^t = MV = (525 \text{ kg})(1000 \text{ g/kg})(15.93 \text{ cm}^3/\text{g}) = 8363250 \text{ cm}^3 = 8.36 \text{ m}^3$$

Problem 2.4 Solution Solution Initial state:

$$P = 45 \text{ bar}, T = 257.41 \text{ °C}, V^L = 1.269 \text{ cm}^3/\text{g}, V^V = 44.037 \text{ cm}^3/\text{g}$$

The specific volume is obtained from the lever rule with $X^L = 0.25$:

$$V = x^L V^L + (1 - x^L)V^V = (0.25)(1.269) + (1 - 0.25)(44.037) = 33.345 \text{ cm}^3/\text{g}$$

a) We know $P = 80$ bar, $V = 33.345 \text{ cm}^3/\text{g}$. From the steam tables we find:

$$T = 375 \text{ °C}, \quad V = 32.222 \text{ cm}^3/\text{g}$$

$$T = 400 \text{ °C}, V = 34.31 \text{ cm}^3/\text{g}$$

By interpolation at $V = 33.345 \text{ cm}^3/\text{g}$ we obtain $T = 388.5 \text{ °C}$.

b) From saturated tables we find:

$$T = 272 \text{ °C}, \quad P = 56.802 \text{ bar}, \quad V = 34.42 \text{ cm}^3/\text{g}$$

$$T = 274 \text{ °C}, \quad P = 58.587 \text{ bar}, \quad V = 33.29 \text{ cm}^3/\text{g}$$

By interpolation at $V = 33.345 \text{ cm}^3/\text{g}$ we find $P = 57.76$ bar.

c) The volume fraction of the liquid, ϕ^L, and the mass fraction of the liquid, x^L, are related as follows:

$$\frac{\text{vol. occupied by liq.}}{\text{vol. occupied by liq.+vol. occupied by vap}} = \frac{x^L V^L}{x^L V^L + x^V V^V}$$

from which,

$$x^L = \frac{V^V \phi^L}{V^L + (V^V - V^L)\phi^L}$$

The saturated volumes are those at the initial state and with $\phi^L = 0.25$ we find

$$x^L = \frac{(44.037)(0.25)}{(1.269) + (44.037 - 1.269)(0.25)} = 0.920429$$

Therefore, the new specific volume in the tank is

$$V' = (0.920429)(1.269) + (1 - 0.920429)(44.037) = 4.6721 \text{ cm}^3/\text{g}$$

If we have mass M initially and mass M' at the end, we can write for the tank volume:

$$V^t = NV = V^t M' \quad \Rightarrow \quad \frac{M'}{M} = \frac{V}{V'}$$

or

$$\frac{M - M'}{M} = \frac{V}{V'} - 1 = \frac{33.345}{4.6721} = 6.14$$

Therefore, we must add 6.14 times the original mass (that's 614%).

Problem 2.5 Solution

P (bar)	0.5	15
V (m³/kg)	1.124	0.031
ρ (kg/m³)	0.88968	32.2581

If we interpolate for V we find

$$V = 0.257138 \text{ m}^3/\text{kg}.$$

If we interpolate for ρ we find

$$\rho = 25.7681 \text{ kg/m}^3 \quad \Rightarrow \quad V = 1/\rho = 0.0388077 \text{ m}^3/\text{kg}.$$

These results are quite different. Which one should we pick?

For the molar volume we have

$$V = \frac{ZRT}{P}.$$

Using $\rho = 1/V$, the molar density is

$$\rho = \frac{P}{ZRT} \tag{2.1}$$

We conclude that while V is *inversely* proportional to P, $1/V$ is proportional, provided that Z does not vary much in the given range. Therefore, we would accept the interpolation in ρ.

Problem 2.6 Solution

a) 198.3 C

b) We first obtain the specific volumes of the saturated liquid and vapor at 15 bar:

$$V^L = 0.0015 \, \text{m}^3/\text{kg}, \quad V^V = 0.1317 \, \text{m}^3/\text{kg}$$

Next we calculate the total mass of each phase:

$$m^L = (0.5 \, \text{m}^3)(0.0015 \, \text{m}^3/\text{kg}) = 434.8 \, \text{kg}$$
$$m^V = (11.5 \, \text{m}^3)(0.1317 \, \text{m}^3/\text{kg}) = 87.3 \, \text{kg}$$

The total mass is
$$m = 434.8 + 87.3 = 522.1 \, \text{kg}$$

c) The quality of the steam is:
$$x^V = \frac{87.3}{522.1} = 0.167$$

d) The specific volume after 87% of the mass is removed is

$$V' = \frac{0.13 \times 522.1}{12 \, \text{m}^3} = 0.1768 \, \text{m}^3/\text{kg}$$

The temperature is obtained by interpolation at 15 bar between 250 °C and 300 °C. We find

$$T' = 320 \, °\text{C}$$

Problem 2.7 Solution a) Since the cooker contains both vapor and liquid, the state is saturated steam. Therefore, $T = T^{\text{sat}} = 120.23\,°C$.

b) From steam tables we obtain the specific volumes of the saturated phasees:

$$V^L = 1.061 \text{ cm}^3/\text{g}, \quad V^V = 885.44 \text{ cm}^3/\text{g}$$

The total volume of the liquid in the cooker is $V^{L,tot} = (0.25)(8)$ liter $= 2000$ cm^3. Therefore, the mass of the liquid is

$$m_L = \frac{V^{L,\text{tot}}}{V^L} = \frac{2000}{1.061} = 1885.0 \text{ g}$$

The volume of the vapor in the cooker is $V^{L,\text{tot}} = (0.75)(8)$ liter $= 6000$ cm^3 and its mass is given by

$$m_V = \frac{V^{L,\text{tot}}}{V^V} = \frac{6000}{885.44} = 6.78 \text{ g}$$

The total mass is

$$m = 1885.0 + 6.78 = 1891.78 \text{ g} = 1.89 \text{ kg}$$

c) The mass fractions of the liquid (x_L), and of the vapor (x_V) are

$$x_L = \frac{1885.0}{1885.0 + 6.78} = 0.9964 = 99.64\%, \quad x_V = 1 - x_L = 0.004 = 0.4\%$$

Even though the vapor occupies 75% of the volume, it only represents 0.4% of the total mass.

d) The quick solution is to take a look at the PV graph. The initial state is at A and the final state, B, is reached by constant-volume cooling. This state is obviously in the two-phase region because the originating state was also inside that region as well. We conclude that $P = P^{\text{sat}}(25\,°C) = 3.166$ kPa. (If, however, state A were in the superheated region, we would be able to tell if B is superheated or vapor/liquid and we would have to do the solution in more detail as shown below.)

Detailed solution: The total volume of the system as well as the specific volume remain constant. The specific volume is

$$V = \frac{V_{\text{cooker}}}{M_{\text{tot}}} = \frac{8000 \text{ cm}^3}{1891.78 \text{ g}} = 4.229 \text{ cm}^3/\text{g}$$

From the saturated steam tables at $25\,°C$ we find, $V^L = 1.003$ cm^3/g, $V^V = 43400$ cm^3/g. The specific volume of the system is between these two values, therefore we still have a saturated system. We conclude that $P = P^{\text{sat}}(25\,°C) = 3.166$ kPa $= 0.03166$ bar.
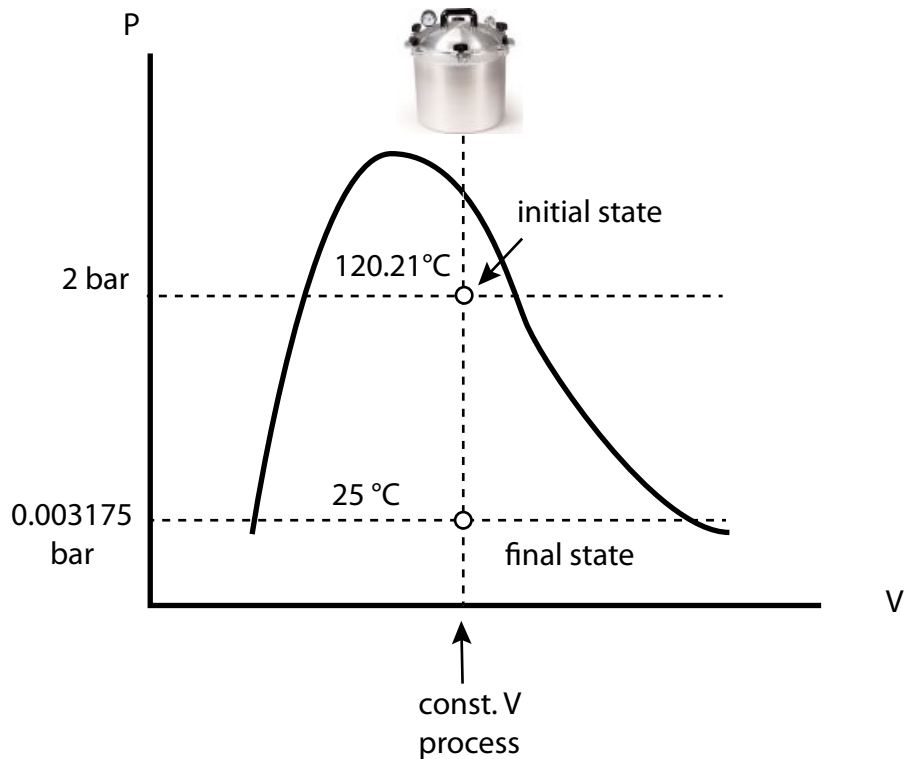
This solution is more general and will work regardless of where the initial state is.

e) When the system has cooled, the outside pressure is 1 bar and the inside pressure is 0.03166 bar. Therefore, the lid remains closed under the action of this pressure difference. The force is

$$F = \pi R^2 (P_{\text{out}} - P_{\text{in}}) = (\pi)(0.2 \text{ m}^2)(1 - 0.03166) \text{ bar} \times 10^5 \text{N/bar} = 12166 \text{ N}$$

To put this force into perspective we calculate the mass whose weight is 12166 N:

$$M = \frac{F}{g} = \frac{12166 \text{ N}}{9.81 \text{ m/s}^2} = 1240 \text{ kg} = 2732 \text{ lb}$$

If you can lift 2700–2800 lb then you could remove that lid! (*Note:* Whether you take the outside pressure to be 1 bar or 1 atm or something similar, the conclusion remains that the required force is indeed very large.

Problem 2.8 Solution

It is very helpful to draw the PV graph, shown below:
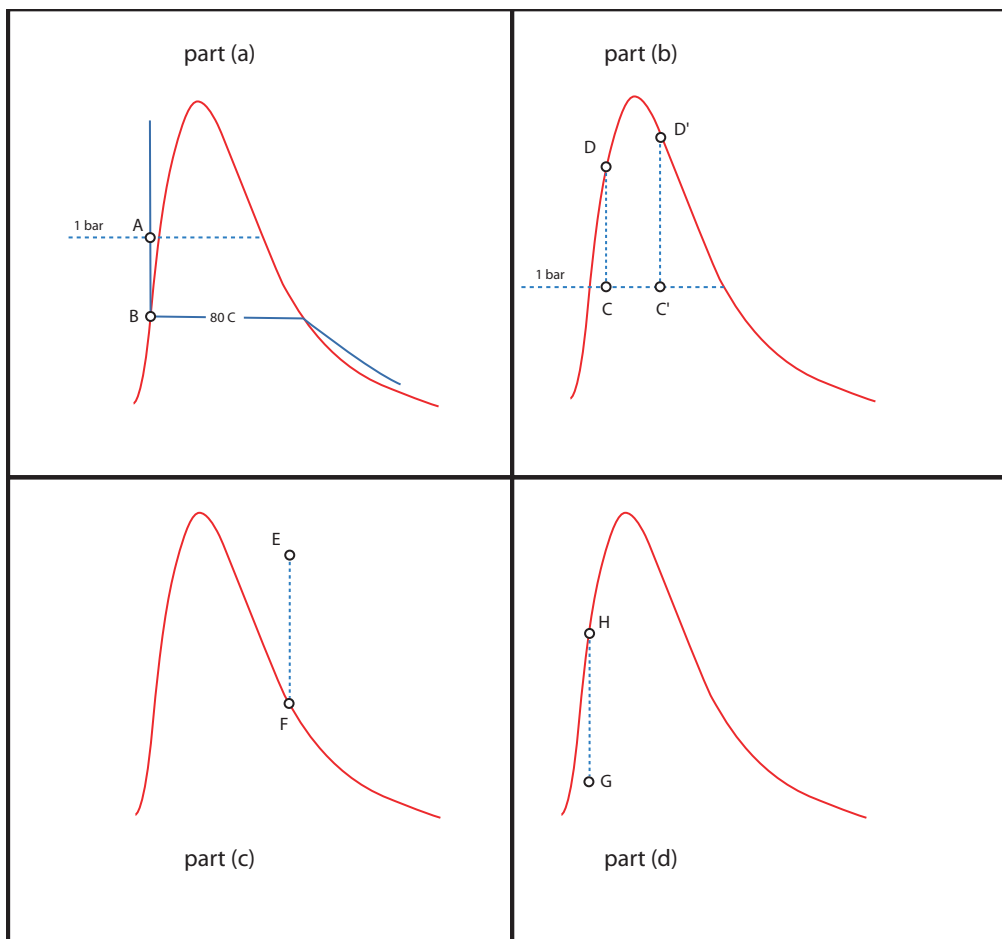
a) The initial state (A) is compressed liquid (80 °C, 1.013 bar). The process is conducted under constant volume. Assuming the isotherm to be vertical, the final state, B, is at the same temperature *and* on the saturation line. Therefore: $T = 80\,°C$, $P = 47.36$ kPa.

Notice that the temperature has not changed. This is a consequence of the fact that we have approximated the isotherm with a vertical line. In reality, the isotherm is not vertical and state B should be at a temperature somewhat below 80 °C. However, the steepness of the isotherm means that this temperature is *very close* to 80 °C. If we had the value of κ and β we could calculate this temperature and would verify that it is indeed extremely close to 80 °C.

b) The initial state is a V/L mixure (state C). The process is under constant volume, therefore, the final state is located at the intersection of the vertical line through C and the saturation line (state D). From steam tables:

$$1 \text{ bar, saturated:} V_L = 1.043, \quad V^V = 1693.7$$

The mass fractions of the liquid and the vapor are:

$$l = \frac{0.5/1.043}{0.5/1.043 + 0.5/1693.7} = 0.99938$$

$$v = 1 - l = 0.00062$$

The specific volume at the initial state is (in cm^3/g)

$$V = (0.99938)(1.043) + (0.00062)(1693.7) = 2.085$$

At the final state: $V = 2.085$, and saturated. From steam tables we find, $T \approx 367\,°C$, $P = 203.13$ bar (saturated liquid).

Note 1: Even though the mass fraction of the vapor is very nearly 0, it would not be correct to set it equal to 0. While v is small, when multiplied by a large V^V it makes a significant contribution to the specific volume of the mixture. If we had set $v \approx$, we would have concluded that the initial state is practically saturated liquid which means that the final pressure is almost 1 bar. Clearly, this approximation misses the right pressure by more than 200 bar!!!

Note 2: In this case the specific volume of the vapor-liquid mixture was very close to the liquid side and for this reason the final state was *liquid*. In other words, under heating the vapor condenses and becomes liquid. If, however, the initial volume was much closer the vapor side (state C'), then heating would produce *vapor*. In this case, heating would cause the liquid to evaporate. That is, after heating the contents of the vessel the final state might either saturated vapor or saturated liquid. Can you establish a criterion for the initial specific volume to determine whether the final state is vapor or liquid?

c) The final state saturated vapor (state F). The process is cooling under constant volume, therefore, the initial state must be somewhere on the vertical line through F and above point F (since cooling implies that the initial state is at higher T). We conclude the initial state is superheated vapor.

d) By similar arguments as above, we determine that the initial state is *vapor/liquid* mixture. Notice that here we are heating a vapor/liquid mixture and as a result the vapor condenses to produce saturated liquid!

Problem 2.9 Solution The specific volume of water under these conditions in the tank is

$$V = \frac{12 \text{ m}^3}{6.2 \text{ kg}} = 1.935 \text{ m}^3/\text{kg}.$$

According to the steam tables, the volume of saturated vapor at 1.4 bar is between 1.694 m^3/kg (at 1 bar) and 1.1594 m^3/kg (at 1.5 bar). The calculated value is higher, therefore, the state is to the right of the saturated vapor and it must be *superheated*.

b) We need an entry in the steam tables such that pressure is 1.4 bar and the specific volume is 1.935 m^3/kg. To locate this state, we interpolated in the steam tables between 1.0 bar and 1.5 bar at various temperatures and construct the table below:

T	150	200	250	300	350	400	450	
V (at 1.0 bar)	1.9367	2.1725	2.4062	2.6389	2.8710	3.1027	3.3342	
V (at 1.4 bar)	1.4158	1.5901	1.7623	1.9335	2.1040	2.2742	2.4442	←
V (at 1.5 bar)	1.2856	1.4445	1.6013	1.7571	1.9123	2.0671	2.2217	

We can now see that the desired value is between 300 °C and 350 °C. By interpolation between these two temperatures we find

$$T = 300 \,°\text{C} + \frac{(350 - 300) \,°\text{C}}{(1.5 - 1.0) \text{ bar}}(1.4 - 1.0) \text{ bar} = 300.6 \text{ C}$$

c) If we add more steam while keeping temperature constant to 300.6 C, pressure will increase and the specific volume will decrease. The vapor will become saturated when the specific volume in the tank is that of saturated vapor at 300.6 C. We obtain this value by interpolation in the saturated steam tables between 300 °C and 302 °C:

T °C	V m^3/kg
300	0.02166
300.593	0.0211498
302	0.01994

The specific volume when the tank is saturated is $V = 0.0211498$ m^3/kg. The total mass is

$$\frac{12 \text{ m}^3}{0.0211498 \text{ m}^3/\text{kg}} 6.2 \text{ kg} = 567.4 \text{ kg}$$

The amount that must be added is

$$(567.4 - 6.2) = 561.2 \text{ kg}$$

Problem 2.10 Solution Solution

The graphs below show the PV in various combinations of linear and logarithmic coordinates and the ZP graph.
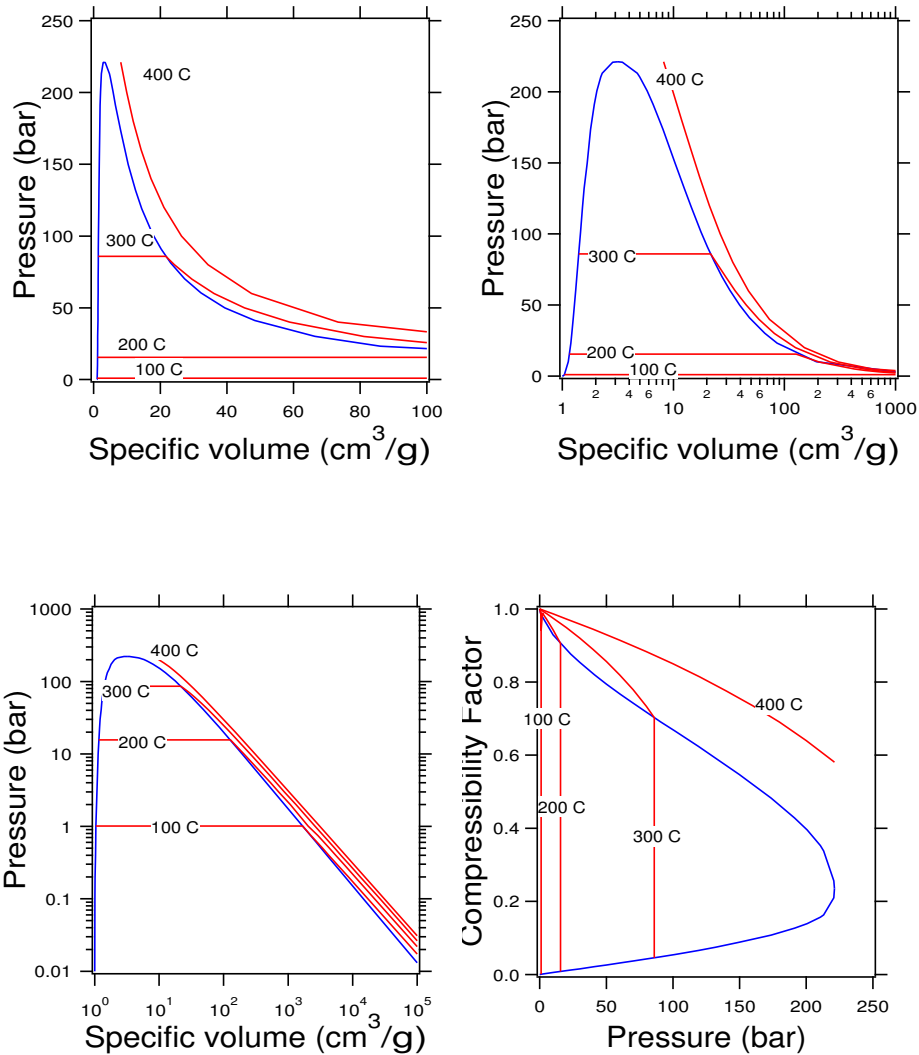
Comments:

- The volumes span a very wide range and in order to see the shape of the saturation line, we must plot only a smaller range. In the above graph, the volume axis ranges from 0 to 100 cm^3/mol.

- By doing the V axis in log coordinates we can now look at a very wide range of values without squeezing the graph into nothingness. Notice that in the log plot the volume goes from 1 to 100,000 cm^3/g.

- The steam tables do not contain data for the compressed liquid region and so our isotherms stop at the saturated liquid. We could extrapolate them into the liquid by drawing them as vertical lines.

- The ZP graph has the familiar look. Notice that the isotherms are better separated on this graph.

Problem 2.11 Solution

a) We find that for ethane,

$$T_c = 305.3\text{K}, \ P_c = 48.72\text{bar}$$

The reduced conditions are

$$T_r = \frac{298.15 \text{ K}}{305.3 \text{ K}} = 0.976, \quad P_r = \frac{10 \text{ bar}}{48.72 \text{ bar}} = 0.21$$

The desired isotherm is between $T_r = 0.95$ and $T_r = 1.0$. By graphical interpolation we find $Z \approx 0.92$. the isotherm is fairly linear between $P_r = 0$ and the value of P_r corresponding to the given pressure, therefore, the truncated virial equation is valid.

b) The reduced conditions are

$$T_r = \frac{244.15 \text{ K}}{305.3 \text{ K}} = 0.80, \quad P_r = \frac{10 \text{ bar}}{48.72 \text{ bar}} = 0.21$$

Z cannot find at $T_r = 0.80$ under the given pressure. therefore, the truncated virial equation is not valid.

c) Since the temperature is $-35°C$, lower than that boiling point, the ethane is liquid. The truncated virial equation is not valid.

Problem 2.12 Solution a) Vapor.

b) The molar mass can be obtained from the relationship between molar volume and density:

$$\rho = \frac{M_m}{V} \quad \Rightarrow \quad M_m = \rho V$$

We know density at two pressures, so we need the molar volume in one of them. We choose the lowest pressure because at 0.01 we are *justified* (below) to assume ideal-gas state:

Justification: The critical pressure is not known but it must be higher than the saturation pressure at 25 C, which is 64.3 bar. That is, the reduced pressure is at most

$$\frac{0.01 \text{ bar}}{64.3 \text{ bar}} = 0.0002$$

From generalized graphs is it clear that at such low reduced pressures the state is essentially ideal.

The molar volume is

$$V = \frac{RT}{P} = \frac{(8.314 \text{ J/mol/K})(298.15 \text{ K})}{0.01 \times 10^5 \text{ Pa}} = 2.47882 \text{ m}^3/\text{mol}$$

The molar mass is

$$M_m = \left(0.177 \text{ kg/m}^3\right)\left(2.47882 \text{ m}^3/\text{mol}\right) = 43.8 \times 10^{-3} \text{ kg/mol}$$

c) The second virial coefficient can be calculated from the truncated virial equation

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

We justify the use of this equation at 25 °C, 20 bar as follows:

Justification: The reduced temperature is $T_r = 0.97$. The reduced pressure is not known but it must be *less* than

$$\frac{20 \text{ bar}}{64.3 \text{ bar}} = 0.31$$

since the critical pressure must be higher than 64.3 bar. From generalized graphs we see that for $T_r \gtrsim 1$, the isotherm in the pressure range $P_r = 0$ up to about 0.31 is quite linear. This of course is a judgement call but is as good as we can do with the information we have.

Solving the truncated virial for B:

$$B = V - \frac{RT}{P}$$

where $V = M_m/\rho$. Using the data at 20 bar with $V = 0.00110239 \text{ m}^3/\text{mol}$ we obtain:

$$B = -1.370 \times 10^{-4} \text{ m}^3/\text{mol}$$

d) We will answer this question using the truncated virial equation

Justification: If the truncated virial is valid at 25 °C, 20 bar, as assumed above, it is valid for all pressures less than 20 bar.

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Solving the truncated virial for V and using $P = 12$ bar:

$$V = \frac{RT}{P} - B = 0.00192866 \text{ m}^3/\text{mol}$$

The number of moles to be stored is

$$n = \frac{20 \text{ kg}}{43.9 \times 10^{-3} \text{ kg/mol}} = 456 \text{ mol}$$

and the volume of the tank is

$$V^{\text{tank}} = (456 \text{ mol})(0.00192866 \text{ m}^3/\text{mol}) = 0.88 \text{ m}^3$$

Problem 2.13 Solution a) We collect the data for this problem:

$$
\begin{aligned}
T_c &= 190.56 \text{ K} \\
P_c &= 45.99 \text{ bar} \\
\omega &= 0.011
\end{aligned}
$$

We calculate the second virial using the Pitzer equation:

$$
\begin{aligned}
T_r &= 1.5646 \\
P_r &= 0.434877 \\
B_0 &= -0.12319 \\
B_1 &= 0.112756 \\
B &= -0.0000420106 \text{ m}^3/\text{mol}
\end{aligned}
$$

The compressibility factor is

$$
Z = \frac{BP_c}{RT} = 0.966104.
$$

b) The molar volume in the tank is

$$
V = \frac{ZRT}{P} = 0.0011974 \text{ m}^3/\text{mol}
$$

The total number of moles is

$$
n = \frac{V^{\text{tank}}}{V} = 835.144 \text{ mol}
$$

c) If we double the number of moles, the new molar volume in the tank is

$$
V_2 = \frac{V^{\text{tank}}}{2n} = \frac{V}{2} = 0.000598699 \text{ m}^3/\text{mol}.
$$

We use the truncate virial to solve for the new pressure P_2 (since temperature is the same as before, the second virial does not need to be recalculated):

$$
\frac{PV}{RT} = 1 + \frac{BP}{RT} \quad \Rightarrow \quad P = \frac{RT}{V - B} = 38.7 \text{ bar}
$$

d) To validate the applicability of the truncated virial we check with the Z^0 graph and notice that isotherms around $T_r = 1.6$ remain linear up to fairly high pressures. The pressure of this problem, $P = 38.7$ bar corresponds to $P_r = 0.84$, which is still within the linear range of the isotherm, as far as we can tell by naked eye.

Summary of results

$$P = \quad 20 \text{ bar}$$
$$T = \quad 298.15v\text{K}$$
$$V_{\text{tank}} \quad 1.0 \text{ m}^3$$
$$T_c = \quad 190.56 \text{ K}$$
$$P_c = \quad 45.99 \text{ bar}$$
$$\omega = \quad 0.011$$
$$T_r = \quad 1.5646$$
$$P_r = \quad 0.434877$$
$$B_0 = \quad -0.12319$$
$$B_1 = \quad 0.112756$$
$$B = \quad -0.0000420106 \text{ m}^3/\text{mol}$$
$$Z = \quad 0.966104$$
$$V = \quad 0.0011974 \text{ m}^3/\text{mol}$$
$$n = \quad 835.144 \text{ mol}$$
$$n_2 = \quad 1670.29 \text{ mol}$$
$$V_2 = \quad 0.000598699 \text{ m}^3/\text{mol}$$
$$P_2 = \quad 38.6886 \text{ bar}$$

Problem 2.14 Solution a) The critical constants and acentric factor of nitrogen are:

$$P_c = 34.0 \text{ bar}, \quad T_c = 126.2 \text{ K}, \quad \omega = 0.038$$

The reduced conditions are

$$P_r = \frac{7 \text{ bar}}{34.0 \text{ bar}} = 0.206, \quad T_r = \frac{110 \text{ K}}{126.2 \text{ K}} = 0.872$$

From Eqs (2.28), (2.29) we have

$$B^0 = 0.083 - \frac{0.422}{0.872^{1.6}} = -0.442395$$

$$B^1 = 0.139 - \frac{0.172}{0.872^{4.2}} = -0.166745$$

$$B^0 + \omega B^1 = -0.442395 - 0.166745 \times 0.038 = -0.448731$$

The second virial coefficient is calculated form Eq. (2.27)

$$B = \frac{RT_c}{P_c}(B^0 + \omega B^1) = (-0.448731)\frac{(8.314 \text{ J/mol K})(126.2 \text{ K})}{34.0 \times 10^5 \text{ Pa}} = -1.3848 \times 10^{-4} \text{ m}^3/\text{mol}$$

The compressibility factor is

$$Z = 1 + \frac{BP}{RT} = 1 - \frac{(1.3848 \times 10^{-4} \text{m}^3/\text{mol})(7 \times 10^5 \text{ Pa})}{(8.314 \text{ J/mol K})(110 \text{ K})} = 0.8940$$

The molar volume is finally calculated to be

$$V = \frac{ZRT}{P} = \frac{(0.8940)(8.314 \text{ J/mol K})(110 \text{ K})}{7 \times 10^5 \text{ Pa}} = 1.168 \times 10^{-3} \text{ m}^3/\text{mol}$$

The mass of nitrogen in the tank

$$m = nM_w = \frac{V^{\text{tank}}}{V}M_w = \frac{5 \text{ m}^3}{1.168 \times 10^{-3} \text{ m}^3/\text{mol}}28.014 \text{ g/mol} = 119.92 \text{ kg}$$

b) In this process the specific volume stays constant. For the two unkowns, P and T, we have the following two equations:

$$\frac{P^{\text{sat}}V}{RT} = 1 + \frac{BP^{\text{sat}}}{RT}$$

$$P^{\text{sat}} = e^{14.9542 - \frac{588.72}{-6.6+T}}$$

These should be solved by trial and error. For example, specify T, solve for P^{sat} from the second equation, solve for V from first equation, and if the answer does not match the known volume, try again. The solution is as following:

T (K)	B	P^{sat} (mmHg)	Z	V (m³/mol)
100	-1.6710×10^{-4}	5715.79	0.846850	9.2393×10^{-4}
90	-2.0477×10^{-4}	2684.39	0.902059	1.8860×10^{-3}
99	-1.7038×10^{-4}	5338.88	0.852655	9.8597×10^{-4}
98	-1.7377×10^{-4}	4979.38	0.858414	1.0535×10^{-3}
97	-1.7726×10^{-4}	4636.94	0.864119	1.1273×10^{-3}
96	-1.8085×10^{-4}	4311.17	0.869766	1.2078×10^{-3}
96.48	-1.7911×10^{-4}	4465.49	0.867063	1.1682×10^{-3}

The volume solved in part a) is 1.168×10^{-3} m^3/mol. Therefore the tempeture is 96.48 K, and the pressure is $P = 4465.49$ mmHg $= 5.95 \times 10^5$ Pa.

c) The reduced state in part (a) is $T_r = 0.87$ and $P_r = 0.206$. The desired isotherm is between $T_r = 0.80$ and $T_r = 0.90$. From a generalized $Z - P$ graph we see that isotherms in this range are fairly linear, therefore the truncated virial is acceptable.

In part (b) we found $T_r = 0.76$ and $P_r = 0.175$. The desired isotherm is between $T_r = 0.70$ and $T_r = 0.80$. Again, the isotherm is fairly linear between $P_r = 0$ and the value of P_r corresponding to the given pressure, therefore, the truncated virial equation is valid.

Problem 2.15 Solution a) The second virial coefficient is directly related to the slope of an isotherm on the ZP graph. Specifically,

$$Z = 1 + \frac{BP}{RT} + \cdots \quad \Rightarrow \quad \frac{BP}{RT} = \left(\frac{\partial Z}{\partial P}\right)_T \bigg|_{P=0}$$

This suggests the following graphical solution: calculate Z from the steam tables at constant T, plot them versus pressure, and obtain the slope of the line near $P = 0$. To facilitate calculations, suppose that P is in kPa, V

From the steam tables at 200 °C we have:

P (kPa)	V (cm^3/g)	Z
1	218350	0.9991
10	21820	0.9984
20	10900	0.9975
30	7267.5	0.9976
40	5447.8	0.9971
50	4356.	0.9966
75	2900.2	0.9953
100	2172.3	0.9940
200	1080.4	0.9887
250	861.98	0.9861
300	716.35	0.9834
350	612.31	0.9806
400	534.36	0.9780

Notice that we had to go up to 400 kPa (4 bar) to see enough change in Z so that we can obtain the slope of the line. The graph is shown below:
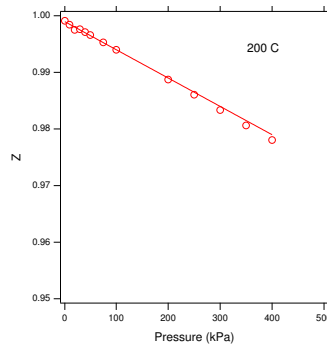
The line shown is tangent to the points at $P = 0$ and its slope is -5.00554×10^{-5}. The easy way to draw this line is to fit a straight line through the points closest to the origin, say below 200 kPa. A smarter way is to use all the points and a *quadratic* equation:

$$f(P) = aP^2 + bP + c$$

Then, the equation of the tangent line at $P = 0$ is (why?)

$$bP + c$$

and its slope is b. Following this procedure we find

$$\text{slope} = -5.00554 \times 10^{-5} \text{ kPa}^{-1} = -5.00554 \times 10^{-8} \text{ Pa}^{-1}$$

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The second virial coefficient is

$$B = (\text{slope})(RT) = (-5.00554 \times 10^{-8} \text{ Pa}^{-1})(8.314 \text{ J/mol K})(473.15 \text{ K}) = -1.969 \times 10^{-4} \text{ m}^3/\text{mol}$$

b) Using the above value of B we can calculate the molar volume of water at 14 bar as follows:

$$\frac{PV}{RT} = 1 + \frac{BP}{RT} \quad \Rightarrow$$

$$
\begin{aligned}
V &= \frac{RT}{P} + B = \frac{(8.314 \text{ J/mol K})(473.15 \text{ K})}{14 \times 10^5 \text{ Pa}} - 1.969 \times 10^{-4} \text{ m}^3/\text{mol} \\
&= 2.613 \times 10^{-3} \text{ m}^3/\text{mol} \\
&= 145.15 \text{ cm}^3/\text{g}
\end{aligned}
$$

The value from the steam tables is 142.94 cm^3/g. This agreement is very good indicating that the truncated virial equation is valid at these conditions.

Problem 2.16 Solution We need the density of methane under these conditions. We will calculate it via the compressibility factor using the Lee-Kesler tables. The critical parameters of methane are:

$$T_c = 190.6 \text{ K}, \quad P_c = 45.99 \text{ bar}, \quad \omega = 0.012$$

The reduced state of methane is

$$T_r = \frac{298.15 \text{ K}}{190.6 \text{ K}} = 1.564, \qquad P_r = \frac{75 \text{ bar}}{45.99 \text{ bar}} = 1.631$$

We must perform a double interpolation in the tables since neither value is listed. The calculation is summarized below:

Interpolations for Z^0   *Interpolations for Z^1*

	P_r				P_r		
	1.5	**1.631**	2.0		1.5	**1.631**	2.0
1.5	0.8689	**0.8595**	0.8328		0.1345	**0.1466**	0.1806
1.564		**0.8811**				**0.1433**	
1.6	0.9	**0.8931**	0.8738		0.1303	**0.1414**	0.1729

Here, numbers in regular font are form the Lee-Kesler tables and those in bold are interpolations. First we interpolate at $T_r = 1.5$ to calculate Z^0 at $P_r = 1.631$ and we obtain 0.8595. Next, we do the same at $T_r = 0.6$ to calculate Z^0 at $P_r = 1.631$ from which we find 0.8931. Finally, we interpolate between these two values to obtain Z^0 at $T_r = 1.564$ to find the value of Z^0 at the desired state. We find

$$Z^0 = 0.8811$$

The procedure is similar for Z^1 where we find

$$Z^1 = 0.1433$$

With these values we calculate the compressibility factor, the molar volume, density, and total volume of the tank:

$$Z = 0.8828, \quad V = 2.92 \times 10^{-4}, \text{ m}^3/\text{mol} \quad \rho = 54.8 \text{ kg/m}^3, \quad V^{\text{tank}} = 18.2 \text{ m}^3$$

Problem 2.17 Solution a) At the given conditions, $T_r = 0.963675$, $P_r = 0.949281$. The state is very close to the critical, therefore, far removed from the ideal-gas state.

b) Using the Lee Kesler method we find

$$Z_0 = 0.381614,$$
$$Z_1 = -0.597626,$$
$$Z = 0.247148,$$
$$V = 0.0000860517 \text{ m}^3/\text{mol}$$

The number of moles in the tank is

$$n = \frac{200 \text{ kg}}{4410^{-3} \text{ kg/mol}} = 4545.45 \text{ mol}$$

and the volume of the tank is

$$V^{\text{tank}} = Vn = 0.391 \text{ m}^3$$

c) At 25 °C, 1 bar, CO_2 is essentially in the ideal-gas state and its molar volume is

$$V_2 = \frac{RT}{P_2} = 0.0243725 \text{ m}^3$$

which means that the moles in th tank are

$$n_2 = \frac{V^{\text{tank}}}{V_2} = 16.048 \text{ mol} \quad \Rightarrow \quad m_2 = 0.706 \text{ kg}$$

We must remove 199.294s kg.

Problem 2.18 Solution

Outline:

a) Calculate P_r and T_r and find the compressibility factor using the Lee-Kesler tables or graphs.

b) With the compressibility factor known, calculate the specific volume and then the total volume of the tank (since the total mass is known).

c) Calculate the new molar volume after 90% (45 kg) is removed. Calculate Z. Since we know Z and T we should be able to obtain P. If we use the Lee-Kesler graph for Z we must do a trial-and-error procedure: choose P, calculate Z, if it doesn't match the known Z try another pressure and continue.

Alternatively, use the truncated virial equation: estimate B using the Pitzer correlation and use

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

to solve for P. Once you have obtained B, confirm that the use of the virial equation was justified.

Calculations

a) The critical parameters of ethylene are:

$$\omega = 0.087$$
$$T_C = 282.3 \text{ K}$$
$$P_C = 50.40 \text{ bar}$$

The reduced temperature and pressure are

$$T_r = \frac{293.15 \text{ K}}{282.3 \text{ K}} = 1.05615, \quad P_r = \frac{80 \text{ bar}}{50.40 \text{ bar}} = 1.5873$$

Checking with the generalized Z graph we see that the state is well-removed from the ideal-gas state.

b) We calculate the compressibility factor using the generalized Lee-Kesler graphs (or by interpolation in tables):

$$Z^0 = 0.322979, \quad Z^1 = 0.0390341 \quad Z = (0.322979) + (0.087)(0.0390341) = 0.326$$

As expected, the compressibility factor is quite below its ideal value. The molar volume of the gas is

$$V = Z\frac{RT}{P} = 0.00010113 \text{ m}^3/\text{mol}$$

The number of moles in the tank is

$$n = \frac{50 \text{ kg}}{28 \times 10^{-3} \text{ kg/mol}} = 1785.71 \text{ mol}$$

and the total volume is

$$V^{\text{tot}} = nV = (1785.71 \text{ mol})(0.00010113 \text{ m}^3/\text{mol}) = 0.181 \text{ m}^3$$

c) The number of moles left in the tank is

$$n' = (0.1)n = 178.6 \text{ mol}$$

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and the new molar volume is

$$V' = \frac{V^{\text{tot}}}{n'} = 0.00101128 \text{ m}^3/\text{mol}$$

We will use the truncated virial since it does not require iterations, but we will have to justify its use afterward.

$$\frac{P'V'}{RT} = 1 + \frac{BP'}{RT} \quad \Rightarrow \quad P' = \frac{RT}{V' - B}$$

We calculate the second virial coefficient using the Pitzer correlation:

$$B^0 = 0.083 - \frac{0.422}{=} - 0.303682$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.00226241$$

$$B = \frac{RT_c}{P_c}(B^0 + \omega B^1) = -0.0001413 \text{ m}^3/\text{mol}$$

Finally, the pressure is

$$P' = \frac{RT}{V' - B} = \underline{21.5 \text{ bar}}$$

Check validity of truncated virial At the final state, $T_r = 1.05615$, $P_r = 0.426709$. If the isotherm at this T_r is sufficiently linear up to $P_r = 0.426709$, the truncated virial is acceptable. The graph in the book looks "linear enough." But we want to be more precise, so we will calculate the compressibility factor form the virial equation and from the Lee-Kesler graphs and will compare:

Using the virial equation:

$$Z = 1 + \frac{BP'}{RT} = 0.877$$

Using the Lee-Kesler tables we find $Z^0 = 0.8677$, $Z^1 = -0.007497$ and

$$Z = (0.8677) + (0.018)(-0.007497) = 0.867$$

Pretty close.

Note: We could have used the ideal-gas law subject to the same condition: after the calculation we should check whether the ideal-gas assumption is correct or not:

$$P' = \frac{RT}{V} = 24.5 \text{ bar}$$

With $T_r = 1.05615$, $P_r = 24.5/50.40 \text{ bar} = 0.486$, the Lee-Kesler charts give $Z = 0.846$. This value is more than 5% way from the ideal-gas state, therefore, we reject the calculation.

Trial and error Here is how to perform a trial-and error solution using the Lee-Kesler tables. We need a starting guess for P - we will use the result fo the ideal-gas calculation, $P_{\text{guess}} = 24.5$ bar. From the Lee-Kesler tables we find

$$Z^0 = 0.846798, \quad Z^1 = -0.00762552, \quad Z_{\text{guess}} = 0.846135, \quad V_{\text{guess}} = 0.00085568 \text{ m}^3/\text{mol}$$

We compare this to the known value $V' = 0.00101128$ m^3/mol by calculating the ratio

$$\frac{V_{\text{guess}}}{V'} = 0.8461$$

The correct pressure must make this ratio equal to 1. Since it is less than 1 (i.e., $V_{\text{guess}} < V'$) we must guess a *lower* pressure, to allow volume to increase. We choose $P_{\text{guess}} = 20$ bar and repeat until the ratio is sufficiently close to 1. The table below summarizes the results of these iterations.

iteration	P_{guess}	Z^0	Z^1	Z_{guess}	V_{guess}	V_{guess}/V'
1	24.5	0.846881	−0.00762573	0.846217	0.000856171	0.84662
2	20	0.877931	−0.00730925	0.877295	0.00108733	1.0752
3	22	0.864336	−0.00754181	0.86368	0.000973139	0.962283
4	21	0.871173	−0.00744249	0.870525	0.00102756	1.0161

The solution is somewhere between 21 and 22 bar. We continue in the same manner if we want to bracket the solution more precisely.

Problem 2.19 Solution We need to calculate densities, i.e. we need V or Z. The ideal-gas law is out of the question because the pressure is too high. Same for the truncated virial equation. We could use either the Lee-Kesler tables or an equation of state. Both methods would be appropriate since krypton is a non-polar compound.

a) We need the density of krypton, so we will first find the compressibility factor at the indicated conditions. From tables we find

$$P_c = 55.02, \quad T_c = 209.4, \quad \omega = 0$$

The given conditions, 20 °C, 110 bar, correspond to reduced conditions

$$P_r = \frac{110}{55.02} = 2.0, \quad T_r = \frac{20 + 273.15}{209.4} = 1.4$$

From the Lee-Kesler tables we find (notice that we don't need Z^1 since the acentric factor is 0)

$$Z = Z^0 = 0.7753$$

The molar volume of Kr is

$$V = \frac{ZRT}{P} = \frac{(0.7753)(8.314 \text{ J/mol K})(293.15 \text{ K})}{110 \times 10^5 \text{ Pa}} = 1.72 \times 10^{-4} \text{ m}^3$$

The number of moles corresponding to 2000 kg of Kr ($M_w = 83.8$) is

$$n = \frac{2000 \times \text{ kg}}{83.8 \times 10^{-3} \text{ kg/mol}} = 23866.3 \text{ mol}$$

and the required volume of the tank is

$$V^{\text{tank}} = nV = (23866.3 \text{ mol})(1.72 \times 10^{-4} \text{ m}^3) = 4.1 \text{ m}^3$$

b) We will calculate the mass in the tank when the pressure is the maximum allowable. At 180 bar, 25 °C, we have

$$P_r = 3.272, \quad T_r = 1.42 \approx 1.4$$

From Lee-Kesler by interpolation:

$$Z = Z^1 = 0.7202 + \frac{0.7761 - 0.7202}{5.0 - 3.0}(3.272 - 3.0) = 0.7278$$

The specific volume is

$$\frac{ZRT}{P} = \frac{(0.7278)(8.314 \text{ J/mol K})(298.15 \text{ K})}{180 \times 10^5 \text{ Pa}} = 1.0 \times 10^{-4} \text{ m}^3$$

and the number of moles of Kr in the tank is

$$n = \frac{V^{\text{tank}}}{V} = \frac{4.1 \text{ m}^3/\text{mol}}{1.0 \times 10^{-4} \text{ m}^3} = 40907.2 \text{ mol}$$

The corresponding mass is

$$M = nM_W = (40907.2 \text{ mol})(83.8 \times 10^{-3} \text{ kg/mol}) = 3428 \text{ kg}$$

That is, 3428 kg is the maximum mass that can be stored at 25 °C without exceeding the safety limit. It is, therefore, safe to store 2500 kg.

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Problem 2.20 We collect the following information for n-butane:

$$P_c = 37.96 \text{ bar}, \quad T_c = 425.1 \text{ K}, \quad \omega = 0.2, \quad V_c = 255 \text{ cm}^3/\text{mol}, \quad Z_c = 0.274$$

a) We need the molar volume of the liquid. Our options are: Lee-Kesler, and Rackett. We choose the Rackett equation because it is known to be fairly accurate while the accuracy of the Lee-Kesler is not very good in the liquid side. Still, if you did the problem using L-K I will consider the solution correct.

$$V = (255 \text{ cm}^3/\text{mol})(0.274)^{(1-293.15/425.1)^{0.2857}} = 100.9 \text{ cm}^3/\text{mol}$$

The moles is

$$M_L = \frac{10^7 \text{ cm}^3}{100.9 \text{ cm}^3/\text{mol}} = 99.1 \times 10^3 \text{ mol}$$

Note: This problem could also be done using the Lee-Kesler. The solution requires more calculations and the final result is very close to the above. This calculation is given at the end of this solution. b) For the volume of the vapor we use Lee-Kesler. The required interpolation is shown below.

	$T_r = 0.7$		
	$P_r = 0.05$	$P_r = 0.0545$	$P_r = 0.1$
Z^0	0.9504	0.9455	0.8958
Z^1	−0.0507	−0.0566	−0.1161

from which we obtain the compressibility factor:
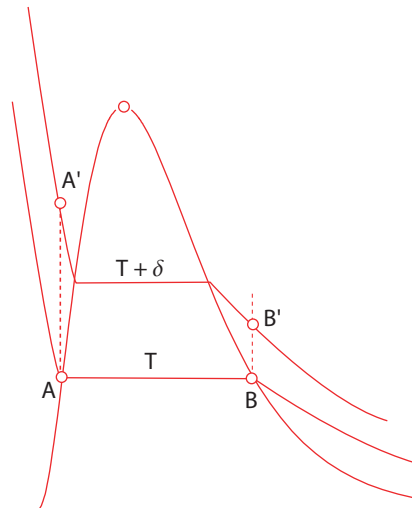
$$Z = 0.9455 + (0.2)(-0.0566) = 0.9342$$

The molar volume is

$$V = \frac{ZRT}{P} = \frac{(0.9342)(8.314)(293.15)}{2.07 \times 10^5} = 1.1 \times 10^{-2} \text{ m}^3/\text{mol}$$

The moles of the vapor are

$$M_V = \frac{10 \text{ m}^3}{1.1 \times 10^{-2} \text{ m}^3/\text{mol}} = 909 \text{ mol}$$

c) To answer this question we take a look at the PV graph.

Both sides of the tank undergo constant-volume processes as indicated by the dashed lines. The graph shows the two states at the initial temperature T, as well as the states at some higher temperature, $T + \delta$. It is obvious that the pressure in the liquid side will always be *higher* than the pressure of the vapor side. Therefore, the pressure of 40 bar will be reached first in the liquid side, causing that alarm to go off.

d) To calculate the temperature at the state we recall that for liquids with constant β and κ, we have

$$\ln \frac{V_2}{V_1} = \beta \Delta T - \kappa \Delta P$$

SInce volume is constant, $V_1 = V_2$ and solving for ΔT we find

$$\Delta T = \frac{\kappa \Delta P}{\beta} = \frac{3.4 \times 10^{-4} \text{ bar}^{-1}(40 - 2.07) \text{ bar}}{2.54 \times 10^{-3} \text{ K}^{-1}} = 5 \,^{\circ}\text{C}$$

The alarm will sound at $T = 20 + 5 = 25 \,^{\circ}\text{C}$. At that point the pressure of the liquid side will be 40 bar while that of the vapor will be not much higher than 2 bar!

Calculation of liquid V using Lee-Kesler:

If you opted to do the calculation using the Lee-Kesler tables, the correct solution is shown below. First we calculate the reduced temperature and pressure.

$$T_r = 0.69 \approx 0.7, \quad P_r = 0.545$$

Note: because the phase is liquid, one must *extrapolate* to $P_r = 0.0545$ from the listed values for the liquid (shown in the tables in italics):

| | $P_r = 0.0545$ | $T_r = 0.7$ | |
		$P_r = 0.2$	$P_r = 0.4$
Z^0	9.45×1^{-3}	0.0344	0.0687
Z^1	-4.1785×10^{-3}	-0.0148	-0.0294

With these values we obtain the following:

$$
\begin{aligned}
Z &= (9.45 \times 1^{-3}) + (0.2)(-4.1785 \times 10^{-3}) = 8.614 \times 10^{-3} \\
V &= \frac{ZRT}{P} = \frac{(8.614 \times 10^{-3})(8.314 \text{ J/mol K})(293.15 \text{ K})}{2.07 \times 10^5 \text{ Pa}} = 1.01 \times 10^{-4} \text{ m}^3/\text{mol} \\
M_L &= \frac{10 \text{ m}^3}{1.01 \times 10^{-4} \text{ m}^3/\text{mol}} = 98.5 \times 10^3 \text{ mol}
\end{aligned}
$$

The answer is very close to that obtained using the Rackett equation but the Lee-Kesler method requires more calculations.

Problem 2.21 Solution Solution a) *Filled with xenon*

We need the volume of the tank which will obtain by first calculating the molar volume of xenon. We will do this calculation using the Pitzer method and the Lee Kesler tables. For xenon:

$$T_c = 289.7 \text{ K}; P_c = 58.4 \text{ bar}; \omega = 0; M_w = 131.30 \text{ g/mol}$$

The reduced temperature and pressure are

$$T_r = \frac{132 + 273.15}{289.7} = 1.39852 \approx 1.4, \quad P_r = \frac{82}{58.4} = 1.4.$$

Interpolating at $T_r = 1.4$ between Pr = 1.2 and Pr = 1.5 we find

$$Z_0 = 0.836436$$

Since $\omega = 0$, $Z = Z^0 = 0.836436$. Using SI units, the molar volume of xenon is

$$V = \frac{ZRT}{P} = (0.836436)(8.314)(405.15)82 \times 10^5 = 3.436 \times 10^4 \text{ m3 /mol}$$

Since the tank contains 10,000 kg, or

$$n = \frac{10,000 \text{ kg}}{131.30 \times 10^{-3} \text{ kg mol}} = 76,161 \text{ mol}$$

the volume of the tank is

$$V^t = nV = 26.16 \text{ m}^3$$

Filled with steam The specific volume of steam in the tank is

$$V = \frac{26.16 \text{ m}^3}{10000 \text{ kg}} = 2.616 \text{ cm}^3\text{/g}$$

At 200 °C, the saturated volumes of water are 1.156 and 127.2 cm3 /g. Since the specific volume lies between the two values, the steam is a saturated vapor/liquid mixture and the pressure is equal to the saturation pressure at 200 °C: $P = 15.45$ bar.

b) If the mass in the tank is reduced to half, the specific volume doubles:

$$V = (2)(2.616) = 5.232 \text{ cm}^3\text{/g}$$

This value is still between that of the saturated vapor and liquid, therefore the pressure remains constant.

Problem 2.22 Solution a) Vapor.

b) At 0.1 bar, 200 C, o-xylene is essentially in the ideal-gas state (why?).

$$V = \frac{RT}{P} = 0.393377 \text{ m}^3/\text{mol}$$

The volume of the tank is

$$V^{\text{tank}} = (200 \text{ mol})(0.393377 \text{ m}^3/\text{mol}) = 39.3 \text{ m}^3. \qquad (2.2)$$

c) At 44.9 bar, 200 C, the reduced temperature an pressure is

$$T_r = 0.75, \quad P_r = 1.2$$

From the Lee-Kesler tables we find

$$Z^0 = 0.84435, \quad Z^1 = 0.0453, Z = 0.8585$$

The molar volume is

$$V_2 = \frac{ZRT}{P_2} = 0.000752133 \text{ m}^3/\text{mol}$$

and the number of moles

$$n = \frac{V^{\text{tank}}}{V_2} = 52301.5 \text{ mol}$$

Problem 2.23 Solution a) We first calculate the coefficient of thermal expansion form the empirical equation given above:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial t}\right)_P \left(\frac{\partial t}{\partial T}\right)$$

where t stands for temperature in celsius and T for temperature in kelvin. Using the polynomial expression given in the problem statement we find

$$\beta = \frac{a_1 + 2a_2 t + 3a_3 t^2}{1 + a_1 t + a_2 t^2 + a_3 t^3}$$

For constant pressure process,

$$\frac{dV}{V} = \beta dT \quad \Rightarrow \quad \frac{V_2}{V_1} = e^{\beta(T_2 - T_1)}$$

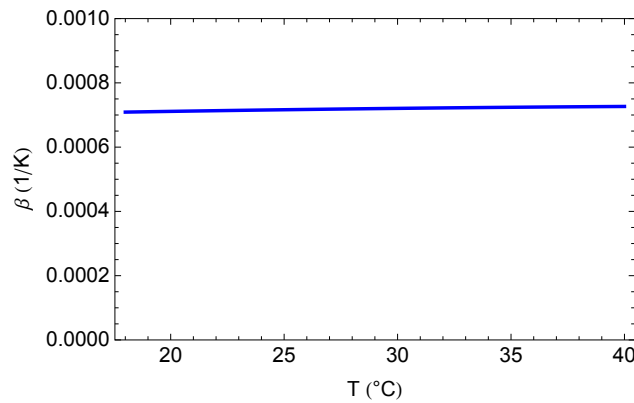For this calculation we will use an average value of β between 18 °C and 40 °C:

$$\beta_{av} = 0.5(\beta_{18} + \beta_{40}) = 0.5(7.09 \times 10^{-4} + 7.27 \times 10^{-4})\ \text{K}^{-1} = 7.18 \times 10^{-4}\ \text{K}^{-1}$$

With this value, the change in volume is

$$\frac{V_2}{V_1} = 1.016$$

or an increase of 1/6%.

Note: We have treated β as nearly constant. To determine the validity of this assumption we make a graph of β in the temperature range of interest:

The coefficient β changes very slowly with temperature, therefore the use of an average value is justified.

b) We start with

$$\frac{dV}{V} = \beta dT - \kappa dP.$$

Assuming the contained to be rigid, volume remains constant, i.e., $dV = 0$. We then integrate the above equation and solve for ΔP:

$$0 = \beta dT - \kappa dP \quad \Rightarrow \quad \kappa \Delta P = \beta \Delta T \quad \Rightarrow \quad \Delta P = \frac{\beta \Delta T}{\kappa}$$

Numerical substitutions:

$$\Delta P = \frac{(7.18 \times 10^{-4}\ \text{K}^{-1})(22\ \text{K})}{52 \times 10^{-6}\ \text{bar}} = 287\ \text{bar}$$

45

Problem 2.24 Solution The numerical results are summarized in the atatched tables:

P=70 bar

```
Fluid    CO2
Tc       304.129    K
Pc       73.74      bar
ω        0.225

T        293.15     K
P        70.        bar
Psat     57.2       bar
Phase    Liquid
```

$$a \quad 0.381864 \quad \frac{Joule\,Meter^3}{Mol^2}$$

$$b \quad 0.0000297087 \quad \frac{Meter^3}{Mol}$$

```
A        0.449994
B        0.085326


Z roots  0.186938


Z        0.186938
```

$$V \quad 0.0000650879 \quad \frac{Meter^3}{Mol}$$

```
moles    7681.92    Mol
mass     338.081    kg
```

P=60 bar

```
T        293.15     K
P        60.        bar
Psat     57.2       bar
Phase    Liquid
```

$$a \quad 0.381864 \quad \frac{Joule\,Meter^3}{Mol^2}$$

$$b \quad 0.0000297087 \quad \frac{Meter^3}{Mol}$$

```
A        0.385709
B        0.0731366


         0.169418
Z roots  0.338098
         0.492484


Z        0.169418
```

$$V \quad 0.000068819 \quad \frac{Meter^3}{Mol}$$

```
moles    7265.44    Mol
mass     319.752    kg
```

50 bar

T	293.15	K
P	50.	bar
Psat	57.2	bar
Phase	Vapor	
a	0.381864	$\frac{\text{Joule Meter}^3}{\text{Mol}^2}$
b	0.0000297087	$\frac{\text{Meter}^3}{\text{Mol}}$
A	0.321424	
B	0.0609471	
	0.160909	
Z roots	0.18658	
	0.652512	
Z	0.652512	
V	0.000318067	$\frac{\text{Meter}^3}{\text{Mol}}$
moles	1572.	Mol
mass	69.1836	kg

Problem 2.25 Solution

First we collect the parameters for isobutane:

$$T_c = 408.1 \text{ K}, \quad P_c = 36.48 \text{ bar}, \quad \omega = 0.181, \quad M_w = 58.123 \times 10^{-3} \text{ kg/mol}$$

We are given $T = 294.26$ K, $P = 4.13793$ bar. With this information we find that the compressibility equation has three real roots:

$$Z_1 = 0.0185567, \quad Z_2 = 0.100577, \quad Z_3 = 0.880866,$$

We know that the phase is liquid (since the given temperature is below the saturation temperature at the given pressure), therefore the correct compressibility factor is the smallest of the three:

$$Z = 0.0185567$$

The corresponding molar volume is

$$V = Z\frac{RT}{P} = (0.0185567)\frac{(8.314 \text{ J/mol K})(294.26 \text{ K})}{4.13793 \times 10^5 \text{ Pa}} = 1.09713 \times 10^{-4} \text{ m}^3/\text{mol}$$
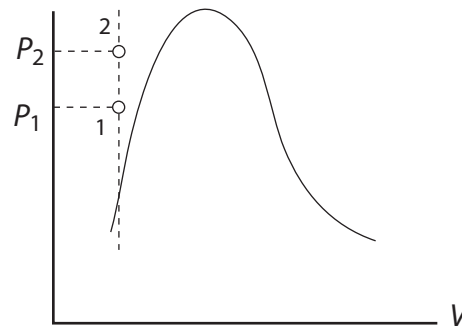
The amount (moles) of isobutane is

$$n = \frac{5000 \text{ kg}}{58.123 \times 10^{-3} \text{ kg/mol}} = 86024.5 \text{ mol}$$

Therefore, the volume of the tank is

$$V^{tank} = (86024.5 \text{ mol})(1.09713 \times 10^{-4} \text{ m}^3/\text{mol}) = 9.44 \text{ m}^3$$

a) Before we solve the problem it is useful to look at the PV graph first.

Since the volume of the tank and the mass of isobutane remain the same, the molar volume also stays the same. In other words, the new state must be on the vertical line that passes through the initial state 1. Since temperature is higher, the final state will be above state 1 (marked as state 2 in the above figure). This is somewhat surprising: one might think that some vapor may be generated since temperature increases. Instead, the system moves firther into the compressed liquid region! This is because heating takes place under *constant volume*.[1]

---

[1] If heating were to take place under constant pressure insead, the final state would move to the right of state 1, possibly creating some vapor.

b) Since the total volume and mass in the tank remain the same, the *molar* volume must also stay the same, namely,

$$V = 1.09713 \times 10^{-4} \text{ m}^3/\text{mol}$$

The pressure can now be calculated directly from the SRK equation:

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

Notice, however, that the parameter a must be recalculated because it depends on temperature. With $T = 308.15$ K we find

$$a = 1.68988 \text{ J m}^3/\text{mol}^2$$

Using this value of a, the previous value of b, and $V = 1.09713 \times 10^{-4}$ m³/mol, the SRK equation gives

$$P = 70.1 \text{ bar}$$

This represents an increase of 66 bar even though temperature increased only by 20 °F! The reason is that isotherms in the compressed liquid state are very steep, resulting in large pressure change under constant-volume heating.

Problem 2.26 Solution

a) At 30 °C, 1 bar the SRK equation has the following three real roots. Since the phase is vapor (why?) we pick the largest root:

$$Z = 0.977286 \quad V = \frac{ZRT}{P} = \underline{0.0246314 \text{ m}^3/\text{mol}}$$

b) At 30 °C, 10 bar the SRK equation has the following three real roots. The phase is liquid (why?), therefore we pick the smallest root:

$$Z = 0.0413973 \quad V = \frac{ZRT}{P} = \underline{0.000104337 \text{ m}^3/\text{mol}}$$

b) At 30 °C, 4.05 bar the SRK equation has the following three real roots. Since the system is saturated, the smallest root is the liquid and largest is the vapor:

$$Z_L = 0.0413973, \quad V_L = \frac{Z_L RT}{P^{\text{sat}}} = \underline{0.000104698 \text{ m}^3/\text{mol}}$$
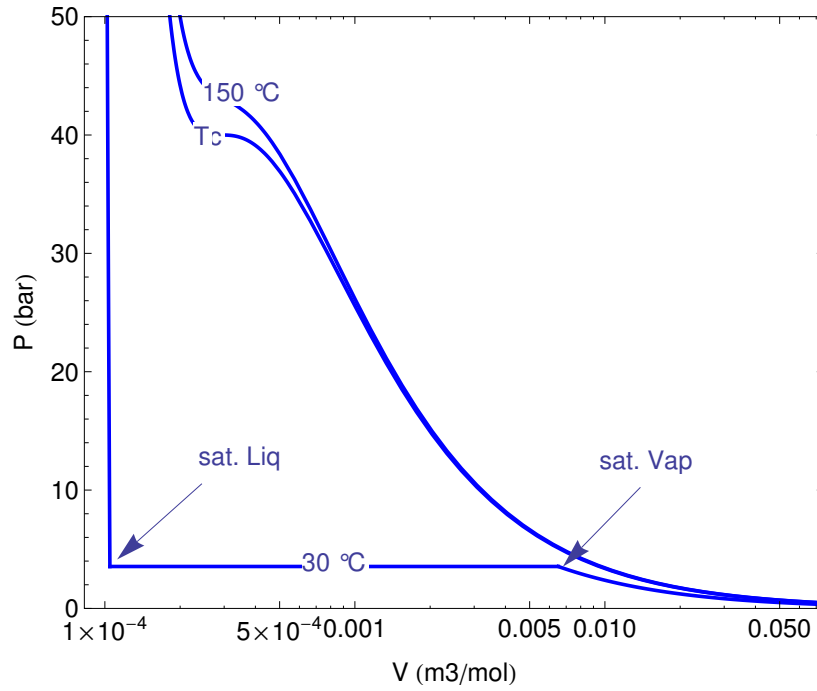
$$Z_V = 0.901582, \quad V_V = \frac{Z_V RT}{P^{\text{sat}}} = \underline{0.00561071 \text{ m}^3/\text{mol}}$$

The literature values from the NIST Web Book are

$$V_L = \underline{0.00010678 \text{ m}^3/\text{mol}} \quad V_V = \underline{0.0055461 \text{ m}^3/\text{mol}}$$

The SRK values are off by -2% (liquid) and 1.2% (vapor). These errors are pretty small.

Problem 2.27 Solution

Note: For maximum readability use semilog coordinates (linear axis for pressure, logarithmic axis for volume).

Problem 2.28 Solution The the general form for the differential of V is

$$\frac{dV}{V} = \beta dT - \kappa dP$$

Using the given expressions for β and κ we have

$$d \ln V = \frac{dT}{T} - \frac{dP}{P} \qquad\qquad \text{[A]}$$

Integration is this differential from V_0, T_0, P_0 to V, T, P is very simple in this case because the variables happen to be separated (each of the three terms contains one variable only). The result is

$$\ln \frac{V}{V_0} = \ln \frac{T}{T_0} - \ln \frac{P}{P_0} \qquad\qquad \text{[B]}$$

The same result is obtained if we adopt an arbitrary integration path, say from T_0, P_0, under constant T to T_0, P, and then under constant P to T, P. As we can easily verify, the differential of the above is indeed equal to Eq. [A]. Equation [B] can be rearranged to write

$$\ln \frac{V}{V_0} = \ln \left(\frac{T}{T_0} \cdot \frac{P_0}{P} \right) \qquad \text{or} \qquad \boxed{\frac{PV}{T} = \frac{P_0 V_0}{T_0}}$$

In other words we have obtained the ideal-gas law.

Based on the final result we can certainly say that this equation of state is not appropriate for liquids. Even before integration, however, we could reach the same conclusion by looking at the T and P dependence of β and κ. The inverse dependence of β on T (and of κ on P) indicates that these parameters vary quite a bit with pressure and temperature. This is a characteristic of gases. The values of κ and β for solids and liquids are typically small numbers and vary much less with temperature and pressure.

Problem 2.29 Solution Using the hint we write:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{1}{V}\right)\bigg/\left(\frac{\partial P}{\partial V}\right)_T$$

Starting with the SRK equation,

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

the derivative wrt V is:

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{a}{V^2}\frac{b+2V}{(b+V)^2} - \frac{RT}{(b-V)^2}$$

Numerical substitutions

$$
\begin{array}{lll}
T = 303.15 & & \text{K} \\
P = 4.05 & & \text{bar} \\
a = 1.60525 & & \text{J/m}^3\text{/mol}^2 \\
b = 0.000075256 & & \text{m}^3\text{/mol} \\
\\
Z_L = 0.0168238 & & \\
V_L = 0.000104698 & & \text{m}^3\text{/mol} \\
(\partial P/\partial V)_T = -1.62039 \times 10^{12} & & \text{bar mol/m}^3 \\
\kappa^L = 0.000589445 & & \text{bar}^{-1} \\
\\
Z_V = 0.901582 & & \\
V_V = 0.00561071 & & \text{m}^3\text{/mol} \\
(\partial P/\partial V)_T = -6.44372 \times 10^7 & & \text{bar mol/m}^3 \\
\kappa^V = 0.276596 & & \text{bar}^{-1}
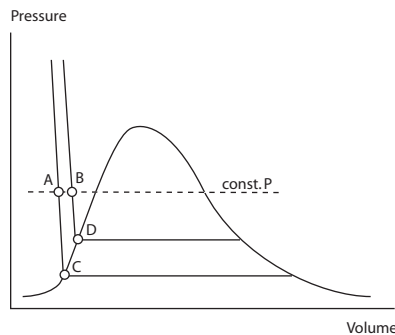\end{array}
$$

Problem 2.30 Solution

a) By definition,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

The partial derivative will be approximated as a finite difference between two states A and B at the same pressure:

$$\left(\frac{\partial V}{\partial T}\right)_P \approx \frac{V_A - V_B}{T_A - T_B}$$

For V we must use a value between V_A and V_B. Choosing $V = (V_A + V_B)/2$, the final result is

$$\beta \approx \frac{2}{V_A + V_B}\frac{V_A - V_B}{T_A - T_B}$$

a) At 25°C, 1 bar, the system is compressed liquid. Assuming the liquid to be incompressible, the required volumes are those of the saturated liquid.

$$
\begin{array}{llll}
T_A & = & 20\,°C & V_A & = & 0.001002\ \mathrm{m^3/kg} \\
T_B & = & 30\,°C & V_B & = & 0.001004\ \mathrm{m^3/kg}
\end{array}
$$

The coefficient of isothermal compressibility is

$$\beta = 1.99402 \times 10^{-4}\ \mathrm{K^{-1}}$$

b) The answer at 10 bar is the same because the assumption of incompressibility implies that the isotherms are vertical and the molar volumes the same as in the previous part.

c) In this case the state is superheated vapor. We select two temperatures around 200 °C and apply the same procedure:

$$
\begin{array}{llll}
T_A & = & 150\,°C & V_A & = & 1.9367\ \mathrm{m^3/kg} \\
T_B & = & 250\,°C & V_B & = & 2.4062\ \mathrm{m^3/kg}
\end{array}
$$

and we find

$$\beta = 2.16215 \times 10^{-3}\ \mathrm{K^{-1}}$$

Problem 2.31 Solution Solution

Assuming isotherms in the compressed liquid region to be vertical, β is calculated as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{\frac{V_1+V_2}{2}}\frac{V_2 - V_1}{T_2 - T_1}$$

where T_1, T_2 are two temperatures around 24 °C, and V_1, V_2, are the volumes of the saturated liquid at these temperatures, to be calculated using the Rackett equation. With $T_1 = 20°C$, $T_2 = 30\ °C$ we find

$$\beta = 1.475 \times 10^{-3}\ \text{K}^{-1}$$

Calculation are shown in the attached notebook.

Rackett Equation

Data for ethanol

In[6]:= **Tc = 513.9 K;**
Pc = 61.48 bar;
ω = 0.645;
Vc = 167 cm^3 / mol;
Zc = 0.24;

Rackett Equation

In[5]:= **V[t_] := Vc Zc$^{(1-t/Tc)^{0.2857}}$**

Calculations

In[14]:= **T1 = (20 + 273.15) K;**
T2 = (30 + 273.15) K;

In[29]:= **V1 = V[T1]**
V2 = V[T2]

$$\beta = \frac{1}{\frac{(V1+V2)}{2}} \frac{V2 - V1}{T2 - T1};$$

Print["β = ", β]

Out[29]= $\dfrac{54.4331 \text{ cm}^3}{\text{mol}}$

Out[30]= $\dfrac{55.2419 \text{ cm}^3}{\text{mol}}$

$\beta = \dfrac{0.00147493}{\text{K}}$

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