Chapter 2: The Physical Properties of Pure Compounds

2-10. The boiler is an important unit operation in the Rankine cycle. This problem further explores the phenomenon of "boiling."

    A. When you are heating water on your stove, before the water reaches 373 K, you see little bubbles of gas forming. What is that, and why does that happen?

    B. Is it possible to make water boil at below 373 K? If so, how?

    C. What is the difference between "evaporation" and "boiling?"

Solution:

A. The small bubbles that form on the bottom of the pot are dissolved air. As temperature goes up, air becomes less soluble in water. Since the water right next to the bottom is hottest, the bubbles usually appear to be coming from particular spots at or near the bottom. Full boil occurs when the temperature of the entire liquid body reaches 373.15 K (if the pressure is atmospheric).

B. It is possible to make water boil below 373 K by lowering the pressure of the surroundings. Water boils at a specific pressure or temperature; if you change the pressure, the boiling temperature also changes. A temperature of less than 373 K requires a pressure less than 0.1 MPa to boil.

C. Evaporation only occurs on the surface of the liquid, but boiling occurs throughout the bulk of the liquid. Another way of thinking of it is that evaporation can only occur if there is already a vapor phase above the liquid (such as the air above an open pot of water on the stove). When a liquid boils, bubbles of vapor form inside the bulk of the liquid; a "new" vapor phase can be created.

Boiling happens when the liquid atoms become so energized that they can overcome the intermolecular forces holding them together which allows them to leave the liquid phase. Evaporation occurs because not all atoms in the liquid are moving at the same speed; even if the average molecular energy isn't sufficient for boiling, the fastest moving particles can overcome intermolecular forces binding them to their nearest neighbors and escape into the vapor phase. Further, atoms in the bulk of liquid experience intermolecular forces from all around them. Atoms at a surface feel forces only from the atoms beneath them. This allows the surface atoms to escape into the vapor phase more readily.

As a specific example, consider water at 298.15 K. We know from everyday experience that this water can evaporate into the air above it; we have seen puddles of water evaporate at ambient temperature. However, a closed container of pure water is all in the

liquid phase at 298.15 K and 0.1 MPa; the water cannot evaporate unless there is a vapor phase (air) for it to evaporate into. Water at 298.15 K will not boil unless the pressure is lowered all the way to 3.17 kPa absolute.

2-11. 10 mol/s of gas flow through a turbine. Find the change in enthalpy that the gas experiences:

    A. The gas is steam, with an inlet temperature and pressure $T = 873.15$ K and $P = 1$ MPa, and an outlet temperature and pressure $T = 673.15$ K and $P = 0.1$ MPa. Use the steam tables.

    B. The gas is steam, with the same inlet and outlet conditions as in part A. Model the steam as an ideal gas using the value of C^*_P given in Appendix D.

    C. The gas is nitrogen, with an inlet temperature and pressure of $T = 300$ K and $P = 1$ MPa, and an outlet temperature and pressure $T = 200$ K and $P = 0.1$ MPa. Use Figure 2-3.

    D. The gas is nitrogen with the same inlet and outlet conditions as in part C. Model the nitrogen as an ideal gas using the value of C^*_P given in Appendix D.

    E. Compare the answers to A and B, and the answers to C and D. Comment on whether they are significantly different from each other, and if so, why.

Solution:

A. Using the steam tables:

$$\widehat{H}_{in} = 3698.6 \frac{kJ}{kg}$$

$$\widehat{H}_{out} = 3278.6 \frac{kJ}{kg}$$

$$\Delta \widehat{H} = \widehat{H}_{out} - \widehat{H}_{in} = 3278.6 \frac{kJ}{kg} - 3698.6 \frac{kJ}{kg}$$

$$\boldsymbol{\Delta \widehat{H} = -420 \frac{kJ}{kg}}$$

B. Using the definition of enthalpy:

$$d\underline{H} = C_P\, dT$$

$$\frac{C^*_P}{R} = A + BT + CT^2 + DT^3 + ET^4$$

Therefore:

$$d\underline{H} = R(A + BT + CT^2 + DT^3 + ET^4)\, dT$$

$$\int_{in}^{out} d\underline{H} = \int_{in}^{out} R(A + BT + CT^2 + DT^3 + ET^4)\, dT$$

$$\Delta\widehat{H} = \widehat{H}_{out} - \widehat{H}_{in}$$

$$= R\left[A(T_{out} - T_{in}) + \frac{B}{2}(T_{out}^2 - T_{in}^2) + \frac{C}{3}(T_{out}^3 - T_{in}^3) + \frac{D}{4}(T_{out}^4 - T_{in}^4)\right.$$
$$\left. + \frac{E}{5}(T_{out}^5 - T_{in}^5)\right]$$

Reading from the appendix, the coefficients are shown in the table below.

Name	Formula	A	B × 10³	C × 10⁵	D × 10⁸	E × 10¹¹
Water	H_2O	4.395	−4.186	1.405	−1.564	0.632

Let us calculate!

$$\Delta\widehat{H} = 8.314\,\frac{kJ}{kmol \cdot K}\left\{4.395[673\ K - 873\ K]\right.$$

$$+ \frac{-4.186 \times 10^{-3}}{2}[(673\ K)^2 - (873\ K)^2]$$

$$+ \frac{1.405 \times 10^{-5}}{3}[(673\ K)^3 - (873\ K)^3]$$

$$+ \frac{-1.564 \times 10^{-8}}{4}[(673\ K)^4 - (873\ K)^4]$$

$$\left.+ \frac{0.632 \times 10^{-11}}{5}[(673\ K)^5 - (873\ K)^5]\right\}$$

$$\Delta\widehat{H} = \left(-7702\,\frac{kJ}{kmol}\right)\left(\frac{1}{18.02}\frac{kmol}{kg}\right)$$

$$\boldsymbol{\Delta\widehat{H} = -427.41\,\frac{kJ}{kg}}$$

C. Based on Figure 2-3:

$$\widehat{H}_{in} = 459\,\frac{kJ}{kg}$$

$$\widehat{H}_{out} = 357\,\frac{kJ}{kg}$$

$$\Delta\widehat{H} = \widehat{H}_{out} - \widehat{H}_{in} = 357\,\frac{kJ}{kg} - 459\,\frac{kJ}{kg}$$

$$\Delta \hat{H} = -102 \, \frac{\text{kJ}}{\text{kg}}$$

D. Using the definition of enthalpy:

$$d\underline{H} = C_P \, dT$$

$$\frac{C_P^*}{R} = A + BT + CT^2 + DT^3 + ET^4$$

Therefore:

$$d\underline{H} = R(A + BT + CT^2 + DT^3 + ET^4) \, dT$$

$$\int_{\text{in}}^{\text{out}} d\underline{H} = \int_{\text{in}}^{\text{out}} R(A + BT + CT^2 + DT^3 + ET^4) \, dT$$

$$\Delta \underline{H} = \underline{H}_{\text{out}} - \underline{H}_{\text{in}}$$
$$= R \left[A(T_{\text{out}} - T_{\text{in}}) + \frac{B}{2}(T_{\text{out}}^2 - T_{\text{in}}^2) + \frac{C}{3}(T_{\text{out}}^3 - T_{\text{in}}^3) + \frac{D}{4}(T_{\text{out}}^4 - T_{\text{in}}^4) \right.$$
$$\left. + \frac{E}{5}(T_{\text{out}}^5 - T_{\text{in}}^5) \right]$$

Name	Formula	A	B × 10³	C × 10⁵	D × 10⁸	E × 10¹¹
Nitrogen	N₂	3.539	−0.261	0.007	0.157	−0.099

Let us calculate!

$$\Delta \underline{H} = 8.314 \, \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \left\{ 3.539[200 \text{ K} - 300 \text{ K}] \right.$$
$$+ \frac{-0.261 \times 10^{-3}}{2}[(200 \text{ K})^2 - (300 \text{ K})^2]$$
$$+ \frac{0.007 \times 10^{-5}}{3}[(200 \text{ K})^3 - (300 \text{ K})^3]$$
$$+ \frac{0.157 \times 10^{-8}}{4}[(200 \text{ K})^4 - (300 \text{ K})^4]$$
$$\left. + \frac{-0.099 \times 10^{-11}}{5}[(200 \text{ K})^5 - (300 \text{ K})^5] \right\}$$

$$\Delta \hat{H} = \left(-2909 \, \frac{\text{kJ}}{\text{kmol}} \right) \left(\frac{1}{28.02} \frac{\text{kmol}}{\text{kg}} \right)$$

$$\Delta \hat{H} = -103.8 \, \frac{\text{kJ}}{\text{kg}}$$

E. The answers from parts A and B differ by ~7 kJ/kg, the answers from parts C and D by ~2 kJ/kg. In both cases the percent error is ~1.7%. Whether this is an acceptable level of error depends upon the application. The differences are attributable to the fact that the ideal gas model is an approximation that is best at low pressure, and these processes included pressures up to 1 MPa.

2-12. Using data from the steam tables in Appendix A, estimate the constant pressure heat capacity of superheated steam at 350 kPa, 473.15 K and at 700 kPa, 473.15 K. Are the answers very different from each other? (NOTE: You may need to use the "limit" definition of the derivative to help you get started.)

Solution:

There is no entry in the steam tables at 350 kPa. Interpolation between the data at 0.3 MPa and 0.5 MPa, and 473.15 K, can be used to find the specific enthalpy at 0.35 MPa and 473.15 K. But what we actually seek is the *change* in specific enthalpy, so we will instead look at the temperatures above and below 473.15 K: 523.15 K and 423.15 K.

First we draw up a table of data on either side of the point of interest at 523.15 K:

	1	1.5	2
y (enthalpy) in kJ/kg	2761.2	?	2752.8
x (pressure) in MPa	0.3	0.35	0.4

Now we interpolate:

$$y = \frac{\left(2761.2\frac{kJ}{kg} - 2752.8\frac{kJ}{kg}\right)(0.35 \text{ MPa} - 0.3 \text{ MPa})}{(0.4 \text{ MPa} - 0.3 \text{ MPa})} + 2761.2\frac{kJ}{kg}$$

$$y = 2757.0\frac{kJ}{kg}$$

Again, we draw up a table…

	1	1.5	2
y (enthalpy) in kJ/kg	2967.9	?	2964.5
x (pressure) in MPa	0.3	0.35	0.4

…and interpolate:

$$y = \frac{\left(2964.5\frac{kJ}{kg} - 2967.9\frac{kJ}{kg}\right)(0.35 \text{ MPa} - 0.3 \text{ MPa})}{(0.4 \text{ MPa} - 0.3 \text{ MPa})} + 2967.9\frac{kJ}{kg}$$

$$y = 2966.2 \frac{kJ}{kg}$$

Constant pressure heat capacity (C_P) can be estimated as the difference in enthalpy divided by the difference in temperature:

$$C_P \approx \frac{\Delta H}{\Delta T} = \frac{2966.2 \frac{kJ}{kg} - 2757.0 \frac{kJ}{kg}}{523.15 \text{ K} - 423.15 \text{ K}}$$

$$C_P \approx 2.092 \frac{kJ}{kg \cdot K}$$

If we attempt to apply a directly analogous procedure at 0.7 MPa there is a complication: water at 0.7 MPa and 423.15 K is a liquid. Since these two intensive properties do not yield a vapor, we must use the enthalpy of saturated vapor at 0.7 MPa. This temperature is 438 K. The enthalpy is

$$\widehat{H}_{P = 0.7 \text{ MPa}, T = 438 \text{ K}} = 2762.8 \frac{kJ}{kg}$$

To find the specific enthalpy of steam at 0.7 MPa and 523 K we interpolate:

	1	**1.5**	**2**
y (enthalpy) in kJ/kg	2957.6	?	2950.4
x (pressure) in MPa	0.6	0.7	0.8

$$y = \frac{\left(2950.4 \frac{kJ}{kg} - 2957.6 \frac{kJ}{kg}\right)(0.7 \text{ MPa} - 0.6 \text{ MPa})}{(0.8 \text{ MPa} - 0.6 \text{ MPa})} + 2957.6 \frac{kJ}{kg}$$

$$y = 2954.0 \frac{kJ}{kg}$$

Calculating the heat capacity by approximation:

$$C_P \approx \frac{\Delta H}{\Delta T} = \frac{2954.0 \frac{kJ}{kg} - 2762.8 \frac{kJ}{kg}}{523.15 \text{ K} - 438 \text{ K}}$$

$$C_P \approx 2.245 \frac{kJ}{kg \cdot K}$$

These answers are fairly similar, but different enough to demonstrate that C_P can in reality be a function of pressure as well as temperature. This is why the distinction between "ideal gas heat capacity" and simply "heat capacity" is important; ideal gas heat capacity is only a function of temperature.

Conceptually, we could get more accurate estimates of C_P by using values $\widehat{H}$ of that were closer to the actual temperature of interest; e.g., 463 K and 483 K instead of 423 K and 523 K. But that data is not included in the available version of the steam table.

2-13. The specific enthalpy of liquid water at typical ambient conditions, like $T = 298.15$ K and $P = 0.1$ MPa, is not given in the steam tables. However, the specific enthalpy of saturated liquid at $P = 0.1$ MPa is given.

    A. Using the approximation that $\hat{C}_P$ for liquid water is constant at 4.19 kJ/kg·K, estimate the specific enthalpy of liquid water at $T = 298.15$ K and $P = 0.1$ MPa.

    B. Compare the answer you obtained in part A to the specific enthalpy of *saturated* liquid water at $T = 298.15$ K.

Solution:

A. Looking up saturated liquid at 0.1 MPa (372.75 K), we find the specific enthalpy ($\hat{H}$) is 417.50 kJ/kg.

Now we integrate the constant heat capacity to estimate the change in specific enthalpy between saturation temperature and the desired temperature.

$$\hat{H}_{298.15\ K} = \hat{H}_{372.75\ K} + \int_{T = 372.75\ K}^{T = 298.15\ K} C_P\, dT$$

$$\hat{H}_{298.15\ K} = 417.5\frac{kJ}{kg} + \left(4.19\ \frac{kJ}{kg \cdot K}\right)(298.15\ K - 372.75\ K)$$

$$\boldsymbol{\hat{H}_{298.15\ K} = 104.43\frac{kJ}{kg}}$$

B. Enthalpy of saturated liquid at 298 K (3.17 kPa) is 104.8 kJ/kg.

This value and our answer from part A are very close. This illustrates that the pressure of a liquid does not have much influence on its enthalpy, at least over a small pressure interval like 0.1 MPa v. 3.17 kPa.

2-14. This problem is an expansion of Example 2-3. The table below lists 10 sets of conditions—5 temperatures at a constant P, and five pressures at a constant T. For each T and P, find:

- The specific volume of steam, from the steam tables
- The specific volume of steam, from the ideal gas law

Comment on the results. Under what circumstances does departure from ideal gas behavior increase?

Temperature	Pressure
473.15 K	0.5 MPa
573.15 K	0.5 MPa
673.15 K	0.5 MPa
773.15 K	0.5 MPa
1273.15 K	0.5 MPa
523.15 K	0.01 MPa
523.15 K	0.1 MPa
523.15 K	0.5 MPa
523.15 K	1.0 MPa
523.15 K	2.5 MPa

Solution:

Here we will display the calculations and reasoning behind the first pair of conditions (**bolded values**):

Temperature	Pressure	$\hat{V}$, steam tables	$\hat{V}$, ideal gas law	% difference
473.15 K	**0.5 MPa**	**0.425 m³/kg**	**0.437 m³/kg**	**2.82**
573.15 K	0.5 MPa	0.523 m³/kg	0.529 m³/kg	1.15
673.15 K	0.5 MPa	0.617 m³/kg	0.621 m³/kg	0.65
773.15 K	0.5 MPa	0.711 m³/kg	0.713 m³/kg	0.28
1273.15 K	0.5 MPa	1.175 m³/kg	1.175 m³/kg	0.00
523.15 K	0.01 MPa	24.136 m³/kg	24.132 m³/kg	-0.02
523.15 K	0.1 MPa	2.406 m³/kg	2.413 m³/kg	0.29
523.15 K	0.5 MPa	0.474 m³/kg	0.483 m³/kg	1.90
523.15 K	1.0 MPa	0.233 m³/kg	0.241 m³/kg	3.43
523.15 K	2.5 MPa	0.087 m³/kg	0.097 m³/kg	11.49

From steam tables, the specific volume of steam at 473 K and 0.5 MPa is 0.425 m³/kg

From the ideal gas law:

$$PV = NRT$$

$$\underline{V} = \frac{RT}{P}$$

$$\underline{V} = \frac{\left(8.314\,\frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}\right)(473.15\text{ K})}{0.5\text{ MPa}} = 0.00788\,\frac{\text{m}^3}{\text{mol}}$$

$$\widehat{V} = (MW)\underline{V} = \left(\frac{1}{18.02}\,\frac{\text{mol}}{\text{g}}\right)\left(0.00788\,\frac{\text{m}^3}{\text{mol}}\right)$$

$$\widehat{V} = \mathbf{0.437}\,\frac{\mathbf{m^3}}{\mathbf{kg}}$$

Departures from ideal gas behavior increase with increasing pressure and with decreasing temperature, since both of these lead to lower volume, and lower volume means more significant intermolecular interaction.

2-15. A refrigeration process includes a compressor, as explained in detail in Chapter 5, because it is necessary to change the boiling point of the refrigerant, which is done by controlling the pressure. Chapter 3 shows that the work required for compression is well approximated as equal to the change in enthalpy. Use Appendix F to find the change in specific enthalpy for each of the scenarios A through C:

   A. Freon 22 enters the compressor as saturated vapor at $P = 0.05$ MPa and exits the compressor at $P = 0.2$ MPa and $T = 293$ K.
   B. Freon 22 enters the compressor as saturated vapor at $P = 0.2$ MPa and exits the compressor at $P = 0.8$ MPa and $T = 333$ K.
   C. Freon 22 enters the compressor as saturated vapor at $P = 0.5$ MPa and exits the compressor at $P = 2$ MPa and $T = 353$ K.
   D. In these three compressors, the inlet and outlet pressures varied considerably, but the "compression ratio" P_{out}/P_{in} was always 4. What do you notice about the changes in enthalpy for the three cases?

Solution:

A. We begin by writing the definition of enthalpy change:

$$\Delta\widehat{H} = \widehat{H}_{out} - \widehat{H}_{in}$$

Repairing to Appendix F, we look up Freon 22's enthalpy at 0.05 MPa and 293 K on the pressure-enthalpy plot.

$$\widehat{H}_{\text{in}} = 383 \ \frac{\text{kJ}}{\text{kg}}$$

We do the same for the outlet conditions and then take the difference to get our answer.

$$\widehat{H}_{\text{out}} = 425 \ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\widehat{H} = \widehat{H}_{\text{out}} - \widehat{H}_{\text{in}} = 425 \ \frac{\text{kJ}}{\text{kg}} - 383 \ \frac{\text{kJ}}{\text{kg}}$$

$$\boldsymbol{\Delta\widehat{H} = 42 \ \frac{\text{kJ}}{\text{kg}}}$$

B. We perform the same process as in part A:

$$\Delta\widehat{H} = \widehat{H}_{\text{out}} - \widehat{H}_{\text{in}}$$

Appendix F supplies the data:

$$\widehat{H}_{\text{in}} = 396 \ \frac{\text{kJ}}{\text{kg}}$$

$$\widehat{H}_{\text{out}} = 445 \ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\widehat{H} = \widehat{H}_{\text{out}} - \widehat{H}_{\text{in}} = 445 \ \frac{\text{kJ}}{\text{kg}} - 396 \ \frac{\text{kJ}}{\text{kg}}$$

$$\boldsymbol{\Delta\widehat{H} = 49 \ \frac{\text{kJ}}{\text{kg}}}$$

C. We perform the same process as in parts A and B:

$$\Delta\widehat{H} = \widehat{H}_{\text{out}} - \widehat{H}_{\text{in}}$$

Appendix F supplies the data:

$$\widehat{H}_{\text{in}} = 405 \ \frac{\text{kJ}}{\text{kg}}$$

$$\widehat{H}_{\text{out}} = 445 \ \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\widehat{H} = \widehat{H}_{\text{out}} - \widehat{H}_{\text{in}} = 445 \ \frac{\text{kJ}}{\text{kg}} - 405 \ \frac{\text{kJ}}{\text{kg}}$$

$$\boldsymbol{\Delta\widehat{H} = 40 \ \frac{\text{kJ}}{\text{kg}}}$$

D. The consistency in compression ratio (always 4) and consistency in $\Delta \hat{H}$ (between 40 kJ/kg and 50 kJ/kg) leads us to believe that the compression ratio (P_{out}/P_{in}) is a major factor influencing enthalpy change (for Freon 22 vapors). Indeed, in real compressors, the compression ratio is far more important than the absolute values of pressure in determining required work.

But you might wonder, why does the temperature change in a compressor, and are the particular combinations of inlet and outlet temperatures and pressures used in this problem realistic? These issues will be explored in Chapter 4, when we begin to discuss *reversible processes* and *efficiencies.*

2-16. The classic way to synthesize ammonia is through the gas phase chemical reaction:

$$N_2 + 3H_2 \rightarrow 2NH_3$$
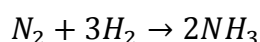
This reaction is carried out at high pressures, most often using an iron catalyst.

    A. Use Equation 2.32 and C_P^* from Appendix D to determine the change in molar enthalpy when nitrogen is compressed from $T = 300$ K and $P = 0.1$ MPa to $T = 700$ K and $P = 20$ MPa.

    B. Repeat part A for hydrogen.

    C. What assumptions or approximations were made in steps A and B? Comment on how valid you think the approximations are.

Solution:

A. Using the definition of enthalpy:

$$d\underline{H} = C_P \, dT$$

$$\frac{C_P^*}{R} = A + BT + CT^2 + DT^3 + ET^4$$

Therefore:

$$d\underline{H} = R(A + BT + CT^2 + DT^3 + ET^4)\, dT$$

$$\int_{in}^{out} d\underline{H} = \int_{in}^{out} R(A + BT + CT^2 + DT^3 + ET^4)\, dT$$

$$\Delta\underline{H} = \underline{H}_{out} - \underline{H}_{in}$$

$$= R\left[A(T_{out} - T_{in}) + \frac{B}{2}(T_{out}^2 - T_{in}^2) + \frac{C}{3}(T_{out}^3 - T_{in}^3) + \frac{D}{4}(T_{out}^4 - T_{in}^4)\right.$$
$$\left. + \frac{E}{5}(T_{out}^5 - T_{in}^5)\right]$$

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Name	Formula	A	B × 10³	C × 10⁵	D × 10⁸	E × 10¹¹
Nitrogen	N₂	3.539	−0.261	0.007	0.157	−0.099

Let us calculate!

$$\Delta \underline{H} = \left(8.314 \frac{kJ}{kmol \cdot K}\right)\left\{3.539[700\ K - 300\ K]\right.$$
$$+ \frac{-0.261 \times 10^{-3}}{2}[(700\ K)^2 - (300\ K)^2]$$
$$+ \frac{0.007 \times 10^{-5}}{3}[(700\ K)^3 - (300\ K)^3]$$
$$+ \frac{0.157 \times 10^{-8}}{4}[(700\ K)^4 - (300\ K)^4]$$
$$\left.+ \frac{-0.099 \times 10^{-11}}{5}[(700\ K)^5 - (300\ K)^5]\right\}$$
$$\Delta \underline{H} = -11,880 \frac{kJ}{kmol}$$

B. Setup is identical to part A, only the heat capacity is different.

Name	Formula	A	B × 10³	C × 10⁵	D × 10⁸	E × 10¹¹
Hydrogen	H₂	2.883	3.681	−0.772	0.692	−0.213

$$\Delta \underline{H} = 8.314 \frac{kJ}{kmol \cdot K}\left\{2.883[700\ K - 300\ K] + \frac{3.681 \times 10^{-3}}{2}[(700\ K)^2 - (300\ K)^2]\right.$$
$$+ \frac{-0.772 \times 10^{-5}}{3}[(700\ K)^3 - (300\ K)^3]$$
$$+ \frac{0.692 \times 10^{-8}}{4}[(700\ K)^4 - (300\ K)^4]$$
$$\left.+ \frac{-0.213 \times 10^{-11}}{5}[(700\ K)^5 - (300\ K)^5]\right\}$$
$$\Delta \underline{H} = \mathbf{11,698} \frac{kJ}{kmol}$$

C. By using Equation 2.32, we assumed that the ideal gas model is valid. When you have an ideal gas, pressure has no effect on enthalpy, which means that we can apply a "constant pressure heat capacity" even in situations where the pressure is not constant.

While the ideal gas model is very reasonable at 0.1 MPa, the final pressure of 20 MPa is much too high a pressure at which to assume the ideal gas model is valid. Indeed, at 700 K and 20 MPa, these compounds are not gases at all, they are supercritical fluids.

2-17. Liquid water enters a steady-state heat exchanger at $P = 1$ MPa and $T = 353.15$ K, and exits as saturated water vapor at $P = 1$ MPa.

   A. Using the steam tables, find the change in specific enthalpy for this process.
   B. Using the approximation that $C_P = 4.19$ kJ/kg·K for liquid water, find the change in enthalpy when liquid water is heated from 353.15 K to its boiling point at $P = 1$ MPa.
   C. How do the answers to parts A and B compare to each other? What is the reason for the difference between them?

Solution:

A. From the steam tables, we find as follows:

$$\hat{H}_{in} = 335.77 \frac{kJ}{kg}$$

$$\hat{H}_{out} = 2777.11 \frac{kJ}{kg}$$

$$\Delta \hat{H} = \hat{H}_{out} - \hat{H}_{in} = 2777.11 \frac{kJ}{kg} - 335.77 \frac{kJ}{kg}$$

$$\boldsymbol{\Delta \hat{H} = 2441.34 \frac{kJ}{kg}}$$

B. The boiling point of water at 1 MPa, according to the steam tables, is 453 K. Thus, the increase in temperature (ΔT) is almost exactly 100 K. To find the enthalpy change, we integrate the heat capacity.

$$\Delta \hat{H} = \int_{T_{in}}^{T_{out}} C_P \, dT$$

The heat capacity is constant in this problem, so it can be factored out of the integrand and the integral taken:

$$\Delta \hat{H} = C_P \int_{T_{in}}^{T_{out}} dT = C_P (T_{out} - T_{in})$$

$$\Delta \hat{H} = C_P \int_{T_{in}}^{T_{out}} dT = C_P (T_{out} - T_{in})$$

$$\Delta \hat{H} = \left(4.19 \frac{kJ}{kg \cdot K} \right) (453 \text{ K} - 353 \text{ K})$$

$$\Delta \hat{H} = 419 \frac{kJ}{kg}$$

C. There is a large difference between the answers to A and B. The value found through the steam tables is the change in specific enthalpy from 353.15 K *liquid* that has been heated to its boiling point (at 1 MPa) and then converted to a *vapor*. This extra heat added to convert a liquid to a vapor is very significant. In part B, we ignored this step—the final state was liquid water at its boiling point (at 1 MPa).

We must always remember, the expression $d\underline{H} = C_P \, dT$ is valid when a temperature change is the only thing occurring in a process—it does not account for changes in pressure or changes in phase.

2-18. One mole of ideal gas is confined in a piston-cylinder device, which is 0.30 m in diameter. The piston can be assumed weightless and frictionless. The internal and external pressures are both initially 101.3 kPa. An additional weight of 4.54 kg is placed on top of the piston, and the piston drops until the gas pressure balances the force pushing the piston downward. The temperature of the gas is maintained at a constant temperature of 300 K throughout the process.

    A. What is the final pressure of the gas?
    B. What is the final volume of the gas?
    C. How much work was done on the gas during the process?

Solution:

A. We know that pressure is force divided by the area it acts upon. The pressure acting on the piston can be found from the force developed by its mass as the acceleration of gravity and the area of the piston. Mathematically:

$$P = \frac{F}{A}$$

$$F = ma$$

$$A = \frac{\pi}{4} D^2$$

$$\therefore P_{\text{weight}} = \frac{4ma}{\pi D^2}$$

Substituting numbers and solving:

$$P_{\text{weight}} = \frac{4}{\pi} \frac{(4.54 \text{ kg}) \left(9.81 \frac{\text{m}}{\text{s}^2}\right)}{(0.30 \text{ m})^2} \left(\frac{\text{N} \cdot \text{s}^2}{\text{kg} \cdot \text{m}}\right) \left(\frac{\text{Pa} \cdot \text{m}^2}{\text{N}}\right)$$

$$P = 630 \text{ Pa}$$

$$P = P_{\text{weight}} + P_{\text{atmosperic}}$$

$$P = 630 \text{ Pa} + 101300 \text{ Pa}$$

$$\mathbf{P = 101930 \text{ Pa} = 101.9 \text{ kPa}}$$

B. For this problem we assume ideal gas behavior and use the ideal gas law:

$$PV = NRT$$

$$V = \frac{NRT}{P}$$

$$V = \frac{(1 \text{ mol}) \left(8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}}\right)(300 \text{ K})}{101930 \text{ Pa}}$$

$$\mathbf{V = 0.0245 \text{ m}^3}$$

C. This one is more involved. We begin with the definition of work of expansion and contraction from Equation 1.22:

$$W_{\text{EC}} = -\int P \, dV$$

Pressure is not constant in this process (the pressure added by the weight is not present at time zero). We must express the pressure in terms of volume for the integral to work. We know that temperature and the amount of substance are constant, so the ideal gas law suggests itself.

$$PV = NRT$$
$$P = \frac{NRT}{V}$$

We also need to know the initial volume of the one mole of gas. Again, using the ideal gas law:

$$V_1 = \frac{NRT}{P_1} = \frac{(1 \text{ mol}) \left(8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}}\right)(300 \text{ K})}{101300 \text{ Pa}} = 0.0246 \text{ m}^3$$

Using Equation 1.22 to quantify work:

$$W_{EC} = - \int_{V_1}^{V_2} P \, dV$$

$$W_{EC} = - \int_{V_1}^{V_2} \frac{NRT}{V} \, dV$$

The numerator is made up entirely of constants, which are factored out:

$$W_{EC} = -NRT \int_{V_1}^{V_2} \frac{1}{V} \, dV$$

Integrating:

$$W_{EC} = -NRT \ln \frac{V_2}{V_1}$$

$$W_{EC} = -(1 \text{ mol}) \left(8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}} \right) (300 \text{ K}) \ln \left(\frac{0.0245 \text{ m}^3}{0.0246 \text{ m}^3} \right)$$

$$W_{EC} = (10.16 \text{ Pa} \cdot \text{m}^3) \left(\frac{\text{J}}{\text{Pa} \cdot \text{m}^3} \right)$$

$$\boldsymbol{W_{EC} = +10.16 \text{ J}}$$

Note the negative sign from the natural log cancels the leading negative in the equation. Physically, work is done ON the gas because the sign is positive (energy is being added to the system)

2-19. Two moles of an ideal gas are confined in a piston-cylinder arrangement. Initially, the temperature is 300 K and the pressure is 1 MPa. If the gas is compressed isothermally to 5 MPa, how much work is done on the gas?

Solution:
Examining Equation 1.22, the definition of work of expansion or contraction, we see we must express pressure as a function of volume since it is not constant in this process.

$$W_{EC} = - \int_{V_1}^{V_2} P \, dV$$

Using the ideal gas law:

$$W_{EC} = -\int_{V_1}^{V_2} \frac{NRT}{V} dV$$

$$W_{EC} = -NRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

Integrating:

$$W_{EC} = -NRT \ln\frac{V_2}{V_1}$$

Finding the initial and final volumes of the system, using the ideal gas law:

$$V_1 = \frac{NRT}{P_1} = \frac{(1 \text{ mol})\left(8.314\frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}\right)(300\text{ K})}{1\text{ MPa}} = 0.0025\text{ m}^3$$

$$V_2 = \frac{NRT}{P_2} = \frac{(1 \text{ mol})\left(8.314\frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}\right)(300\text{ K})}{5\text{ MPa}} = 0.0005\text{ m}^3$$

Inserting and solving for W_{EC}:

$$W_{EC} = -(1\text{ mol})\left(8.314\frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}\right)(300\text{ K})\ln\left(\frac{0.0005\text{ m}^3}{0.0025\text{ m}^3}\right)$$

$$W_{EC} = (4014\text{ Pa}\cdot\text{m}^3)\left(\frac{\text{J}}{\text{Pa}\cdot\text{m}3}\right)$$

$$\boldsymbol{W_{EC} = +4\text{ kJ}}$$

2-20. A gas is stored in an isochoric, refrigerated tank that has $V = 5$ m^3. Initially, the gas inside the tank has $T = 288$ K and $P = 0.5$ MPa, while the ambient surroundings are at 298 K and atmospheric pressure. The refrigeration system fails, and the gas inside the tank gradually warms to 298 K.

   A. Find the final pressure of the gas, assuming it is an ideal gas.
   B. Find the final pressure of the gas, assuming the gas is described by the van der Waals equation of state, with $a = 0.08$ m$^6\cdot$Pa/mol^2 and $b = 10^{-4}$ m^3/mol.
   C. For the cases in parts A and B, how much work was done by the gas on the surroundings?

Chapter 2: The Physical Properties of Pure Compounds

Solution:

A. Using the ideal gas law twice solves the problem:

$$\frac{P_1 V_1}{P_2 V_2} = \frac{N_1 R T_1}{N_2 R T_2}$$

For an isochoric system, volume is constant. For a closed system (which we assume based on the description), the amount of substance must be constant. The gas constant is always the same.

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

$$P_2 = P_1 \frac{T_2}{T_1}$$

$$P_2 = (0.5 \text{ MPa}) \left(\frac{298 \text{ K}}{288 \text{ K}}\right)$$

$$\boldsymbol{P_2 = 0.517 \text{ MPa}}$$

B. Find the molar volume of gas at the initial temperature and pressure, using the van der Waals equation:

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

$$5 \text{ MPa} = \frac{\left(8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}}\right)(288 \text{ K})}{\underline{V} - \left(10^{-4} \frac{\text{m}^3}{\text{mol}}\right)} - \frac{\left(0.08 \frac{\text{m}^6 \cdot \text{Pa}}{\text{mol}^2}\right)}{\underline{V}^2}$$

Solving this cubic equation for molar volume yields three answers, only one of which is real. We use the methods of the chapter for identifying real values from the equation:

$$\underline{V} = 0.004544 \frac{\text{m}^3}{\text{mol}}$$

Since system is closed and isochoric, N, V and $\underline{V}$ are all constant. At final conditions:

$$P = \frac{\left(8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})}{\left(0.004544 \frac{\text{m}^3}{\text{mol}}\right) - \left(10^{-4} \frac{\text{m}^3}{\text{mol}}\right)} - \frac{\left(0.08 \frac{\text{m}^6 \cdot \text{Pa}}{\text{mol}^2}\right)}{\left(0.004544 \frac{\text{m}^3}{\text{mol}}\right)^2}$$

$$P = 0.519 \text{ MPa}$$

No work was done on the gas by the environment. Heat was added, but there was no expansion or contraction, and therefore no W_{EC}.

2-21. Biosphere II is an experimental structure that was designed to be an isolated ecological space, intended for conducting experiments on managed, self-contained ecosystems. Biosphere II (so named because the earth itself was regarded as the first "Biosphere") is covered by a rigid dome. One of the engineering challenges in designing Biosphere II stemmed from temperature fluctuations of the air inside the dome. To prevent this from resulting in pressure fluctuations that could rupture the dome, flexible diaphragms called "lungs" were built into the structure. These "lungs" expanded and contracted so that changes in air volume could be accommodated while pressure was maintained constant.

For the purposes of this problem, assume that air is an ideal gas, with heat capacity equal to a weighted average of the ideal gas heat capacities of nitrogen and oxygen:

$$C_{P\,\text{air}}^* = 0.79 C_{P\,\text{N}_2}^* + 0.21 C_{P\,\text{O}_2}^*$$

In parts A and B, suppose the volume of air contained within the Biosphere II was 125,000 m^3, there were no lungs, and the pressure of the air was 100 kPa when the temperature was 294 K.

   A. What air pressure would occur at a temperature of 255 K?
   B. What air pressure would occur at a temperature of 314 K?

For parts C-E assume the Biosphere II does have lungs, and that the total volume of air inside the dome is 125,000 m^3 *when the lungs are fully collapsed.*

   C. If the lungs are designed to maintain a constant pressure of 0.1 MPa at all temperatures between 255 K and 314 K, what volume of air must the lungs hold when fully expanded?
   D. If the temperature inside the dome increases from 255 K and 314 K at a constant $P = 0.1$ MPa, what change in internal energy does the air undergo?
   E. If the temperature inside the dome increases from 255 K and 314 K at a constant $P = 0.1$ MPa, and the lungs are sized as calculated in part C, give your best estimate of the work done by the lungs on the surroundings.

Solution:

A. At these conditions, we can assume ideal gas behavior. Consider N constant (closed system), V constant (given), and R constant (always true). So:

$$\frac{P_1 V_1}{P_2 V_2} = \frac{N_1 R T_1}{N_2 R T_2}$$

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

$$P_2 = P_1 \frac{T_2}{T_1}$$

$$P_2 = (0.1 \text{ MPa}) \left(\frac{255 \text{ K}}{294 \text{ K}} \right)$$

$$\boldsymbol{P_2 = 0.0867 \text{ MPa}}$$

B. Repeating part A, but for a different tempereature:

$$\frac{P_1 V_1}{P_2 V_2} = \frac{N_1 R T_1}{N_2 R T_2}$$

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

$$P_2 = P_1 \frac{T_2}{T_1}$$

$$P_2 = (0.1 \text{ MPa}) \left(\frac{313 \text{ K}}{294 \text{ K}} \right)$$

$$\boldsymbol{P_2 = 0.106 \text{ MPa}}$$

C. To solve this, we again assume ideal gas applicability, and solve for the volume of air in the system. To solve for this we need N_{min}. Since the system is closed, N is constant and can be found from V_{min}. The minimum volume occurs at the minimum temperature

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

$$N = \frac{(0.1 \text{ MPa})(125,000 \text{ m}^3)}{\left(8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}} \right)(252 \text{ K})} = 5.90 \text{ Mmol}$$

For the same N and P, and the maximum temperature:

$$V = \frac{NRT}{P} = \frac{(5.90 \text{ Mmol}) \left(8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}} \right)(313 \text{ K})}{0.1 \text{ MPa}} = 153,000 \text{ m}^3$$

Thus the lungs need to be able to hold $153,000 - 125,000 = 28,000 \text{ m}^3$ of air when fully expanded.

D. Since this is being modeled an ideal gas, internal energy is dependent only on temperature, *vide* Equation 2.21:

$$d\hat{U} = \hat{C}_V \, dT$$

We do not have the heat capacity at constant volume for the air, but we do have the constant pressure heat capacity. As Example 2-4 showed,

$$C_P^* = C_V^* + R$$

So,

$$\int d\hat{U} = \int \hat{C}_V \, dT$$

$$\int d\hat{U} = \int (C_P^* - R) \, dT$$

$$\int d\hat{U} = \int_{T_{in}}^{T_{out}} \left(0.79 C_{P\,N_2}^* + 0.21 C_{P\,O_2}^* - R \right) dT$$

$$\int d\hat{U} = 0.79 \int_{T_{in}}^{T_{out}} C_{P\,N_2}^* \, dT + 0.21 \int_{T_{in}}^{T_{out}} C_{P\,O_2}^* \, dT - R \int_{T_{in}}^{T_{out}} dT$$

Integrating the heat capacity for nitrogen:

$$\frac{C_P^*}{R} = A + BT + CT^2 + DT^3 + ET^4$$

Looking up data in the appendix:

Name	Formula	A	B × 10³	C × 10⁵	D × 10⁸	E × 10¹¹
Nitrogen	N₂	3.539	-0.261	0.007	0.157	-0.099

$$C_{P\,N_2}^* = R \int_{255\,K}^{313\,K} (A + BT + CT^2 + DT^3 + ET^4) \, dT$$

$$C_{P\,N_2}^* = \left(8.314 \frac{J}{mol \cdot K} \right) \Big\{ 3.539[313\,K - 255\,K]$$

$$+ \frac{-0.261 \times 10^{-3}}{2} [(313\,K)^2 - (255\,K)^2]$$

$$+ \frac{0.007 \times 10^{-5}}{3} [(313\,K)^3 - (255\,K)^3]$$

$$+ \frac{0.157 \times 10^{-8}}{4} [(313\,K)^4 - (255\,K)^4]$$

$$+ \frac{-0.099 \times 10^{-11}}{5} [(313\,K)^5 - (255\,K)^5] \Big\}$$

$$0.79 \int_{255 \text{ K}}^{313 \text{ K}} C_{P\,N_2}^* \, dT = 1341.26 \frac{J}{mol}$$

Now for oxygen:

Name	Formula	A	B × 10³	C × 10⁵	D × 10⁸	E × 10¹¹
Oxygen	O₂	3.630	-1.794	0.658	-0.601	0.179

$$C_{P\,O_2}^* = R \int_{255 \text{ K}}^{313 \text{ K}} (A + BT + CT^2 + DT^3 + ET^4) \, dT$$

$$C_{P\,O_2}^* = \left(8.314 \frac{J}{mol \cdot K}\right) \left\{ 3.630[313 \text{ K} - 255 \text{ K}] \right.$$
$$+ \frac{-1.794 \times 10^{-3}}{2} [(313 \text{ K})^2 - (255 \text{ K})^2]$$
$$+ \frac{0.658 \times 10^{-5}}{3} [(313 \text{ K})^3 - (255 \text{ K})^3]$$
$$+ \frac{-0.601 \times 10^{-8}}{4} [(313 \text{ K})^4 - (255 \text{ K})^4]$$
$$\left. + \frac{-0.179 \times 10^{-11}}{5} [(313 \text{ K})^5 - (255 \text{ K})^5] \right\}$$

$$0.21 \int_{255 \text{ K}}^{313 \text{ K}} C_{P\,N_2}^* \, dT = 359.28 \frac{J}{mol}$$

Don't forget the last term in on the right hand side:

$$-R \int_{255 \text{ K}}^{313 \text{ K}} dT = \left(8.314 \frac{J}{mol \cdot K}\right)(313 \text{ K} - 255 \text{ K}) = 485 \frac{J}{mol}$$

Combining all three integration results:

$$\int d\widehat{U} = 0.79 \int_{255 \text{ K}}^{313 \text{ K}} C_{P\,N_2}^* \, dT + 0.21 \int_{255 \text{ K}}^{313 \text{ K}} C_{P\,N_2}^* \, dT - R \int_{255 \text{ K}}^{313 \text{ K}} dT$$

$$\Delta\widehat{U} = 1341.26 \frac{J}{mol} + 359.28 \frac{J}{mol} - 485 \frac{J}{mol}$$

$$\Delta\widehat{U} = 1215.5 \frac{J}{mol}$$

Finally, converting to internal energy (instead of specific internal energy):

$$\Delta U = \left(1215.5\,\frac{J}{mol}\right)(5.90\ \text{Mmol})$$
$$\Delta U = \mathbf{7.17\ GJ}$$

E. Work of expansion and contraction is solved for using Equation 1.22:

$$W_{EC} = -\int P\ dV$$

Pressure is constant, so the integral integrates to ΔV:

$$W_{EC} = -P\int dV = -P\Delta V$$

$$W_{EC} = -(0.1\ \text{MPa})(28{,}000\ \text{m}^3)\left(\frac{J}{Pa \cdot m^3}\right)$$

$$\boldsymbol{W_{EC} = -2.8\ GJ}$$

Use the following data for problems 2-22 through 2-26. A compound has:

- A molecular weight of 50 kg/kmol
- A normal melting point of 300 K
- A normal boiling point of 350 K
- A constant heat capacity in the solid phase of $C_P = 3000$ J/kg·K
- A constant heat capacity in the liquid phase of $C_P = 3600$ J/kg·K
- A constant density in the solid phase of $\rho = 640$ kg/m³
- A constant density in the liquid phase of $\rho = 480$ kg/m³
- An ideal gas heat capacity of $C_P{}^* = 4186.8 - 6.28T + 13.56\times10^{-3}T^2$ J/kg·K, with T representing the temperature in Kelvin.
- An enthalpy of fusion $\Delta\widehat{H}_{fus} = 175$ kJ/kg at atmospheric pressure
- An enthalpy of vaporization $\Delta\widehat{H}_{vap} = 300$ kJ/kg at atmospheric pressure

2-22. Estimate the change in $\widehat{U}$ when this compound melts at atmospheric pressure.

Solution:

Beginning with Equation 2.14:

$$\widehat{H} = \widehat{U} + P\widehat{V}$$

Since we are at a constant pressure, we can expand this to:

$$\Delta\hat{H} = \Delta\hat{U} + P\Delta\hat{V}$$

Rearranging this to solve for change in specific internal energy:

$$\Delta\hat{U} = \Delta\hat{H} - P\Delta\hat{V}$$

If the change (the deltas) is melting at atmospheric pressure, the change in enthalpy is the heat of fusion:

$$\Delta\hat{U} = \Delta\hat{H}_{\text{fus}} - P\Delta\hat{V}$$

Now we can substitute in values, noting that specific volume is the inverse of mass density:

$$\Delta\hat{U} = \Delta\hat{H}_{\text{fus}} - P\left(\frac{1}{\rho_2} - \frac{1}{\rho_1}\right)$$

$$\Delta\hat{U} = 175\,\frac{\text{kJ}}{\text{kg}} - (0.1\text{ MPa})\left(\frac{1}{480\,\frac{\text{kg}}{\text{m}^3}} - \frac{1}{640\,\frac{\text{kg}}{\text{m}^3}}\right)\left(\frac{\text{J}}{\text{Pa}\cdot\text{m}^3}\right)\left(\frac{10^6\text{ Pa}}{\text{MPa}}\right)$$

$$\Delta\boldsymbol{\hat{U}} = 175 - 0.05 = \boldsymbol{174.95}\,\frac{\textbf{kJ}}{\textbf{kg}}$$

2-23. What is the change in internal energy when this compound boils at atmospheric pressure?

Solution:

Beginning with Equation 2.14:

$$\hat{H} = \hat{U} + P\hat{V}$$

Since we are at a constant pressure, we can expand this to:

$$\Delta\hat{H} = \Delta\hat{U} + P\Delta\hat{V}$$

Rearranging this to solve for change in specific internal energy:

$$\Delta\hat{U} = \Delta\hat{H} - P\Delta\hat{V}$$

If the change (the deltas) is melting at atmospheric pressure, the change in enthalpy is the heat of vaporization:

$$\Delta\hat{U} = \Delta\hat{H}_{\text{vap}} - P\left(\hat{V}_{\text{v}} - \hat{V}_{\text{L}}\right)$$

Where the subscripts on the specific volumes indicate the vapor and liquid states.

Next, we assume that the vapor phase specific volume can be described by the ideal gas law:

$$\hat{V}_v = \frac{\underline{V}}{MW} = \frac{RT}{P[MW]}$$

Combining:

$$\Delta\hat{U} = \Delta\hat{H}_{vap} - P\left(\frac{RT}{P[MW]} - \hat{V}_L\right)$$

Inserting values:

$$\Delta\hat{U} = 300\,\frac{kJ}{kg} - (0.1\,MPa)\left(\frac{\left[8.314\frac{Pa\cdot m^3}{mol\cdot K}\right][350\,K]}{[0.1\,MPa]\left[0.05\frac{kg}{mol}\right]} - \frac{1}{480\frac{kg}{m^3}}\right)\left(\frac{J}{Pa\cdot m^3}\right)$$

$$\Delta\hat{U} = 241.8\,\frac{kJ}{kg}$$

2-24. When one kmol is heated from 269 K to 366 K at a constant pressure of $P = 101.325$ kPa:

    A. Give your best estimate of the change in enthalpy
    B. Give your best estimate of the change in internal energy

Solution:

A. This process can be broken down into five steps:
$$\Delta H = \Delta H_{269\,K\to300\,K} + \Delta H_{fus} + \Delta H_{300\,K\to350\,K} + \Delta H_{vap} + \Delta H_{350\,K\to366\,K}$$

$$\frac{\Delta H}{M} = \Delta\hat{H} = \int_{269\,K}^{300\,K} C_{P,solid}\,dT + \Delta\hat{H}_{fus} + \int_{300\,K}^{350\,K} C_{P,liquid}\,dT + \Delta\hat{H}_{vap}$$
$$+ \int_{350\,K}^{366\,K} C_{P,gas}^*\,dT$$

$$\frac{\Delta H}{M} = \int_{269\,K}^{300\,K}\left(3\frac{kJ}{kg\cdot K}\right)dT + 175\frac{kJ}{kg} + \int_{300\,K}^{350\,K}\left(3.6\frac{kJ}{kg\cdot K}\right)dT + 300\frac{kJ}{kg}$$
$$+ \int_{350\,K}^{366\,K}(4186.8 - 6.28T + (13.56\times10^{-3})T^2)\,dT$$
$$\frac{\Delta H}{M} = 93\frac{kJ}{kg} + 175\frac{kJ}{kg} + 180\frac{kJ}{kg} + 300\frac{kJ}{kg} + 66.2\frac{kJ}{kg}$$
$$\frac{\Delta H}{M} = 814\frac{kJ}{kg}$$

$$\Delta H = \left(814\,\frac{\text{kJ}}{\text{kg}}\right)(1\text{ kmol})\left(50\,\frac{\text{kg}}{\text{kmol}}\right)$$
$$\Delta H = \mathbf{40.7\ MJ}$$

B. Give your best estimate of the change in internal energy.

$$\Delta\hat{U} = \Delta\hat{H} - P\Delta\hat{V}$$
$$\Delta\hat{U} = \Delta\hat{H} - P\left(\hat{V}_\text{v} - \hat{V}_\text{S}\right)$$

Where the subscripts on the specific volumes indicate the vapor and liquid states.

Next, we assume that the vapor phase specific volume can be described by the ideal gas law:

$$\hat{V}_\text{v} = \frac{V}{MW} = \frac{RT}{P[MW]}$$

Combining:

$$\Delta\hat{U} = \Delta\hat{H} - P\left(\frac{RT}{P(MW)} - \hat{V}_\text{S}\right)$$

Inserting values:

$$\Delta\hat{U} = 814\,\frac{\text{kJ}}{\text{kg}} - 0.101325\text{ MPa}\left(\frac{\left[8.314\,\frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}\right][366\text{ K}]}{[0.101325\text{ MPa}]\left[0.05\,\frac{\text{kg}}{\text{mol}}\right]} - \frac{1}{640\,\frac{\text{kg}}{\text{m}^3}}\right)$$

$$\Delta\hat{U} = \mathbf{753\,\frac{kJ}{kg}}$$

2-25. The compound is initially at 278 K. If the pressure is constant at $P = 101.325$ kPa throughout the process, and the specific enthalpy of the compound is increased by 815 kJ/kg, what is the final temperature?

Solution:

The transition from solid at 278 K to vapor at unknown temperature T can be modeled in five steps: heating the solid to 300 K, melting the solid, heating the liquid to 350 K, boiling the liquid, and heating the vapor to T:

$$\Delta H = \Delta H_{269\text{ K}\to300\text{ K}} + \Delta H_\text{fus} + \Delta H_{300\text{ K}\to350\text{ K}} + \Delta H_\text{vap} + \Delta H_{350\text{ K}\to366\text{ K}}$$

$$\frac{\Delta H}{M} = \Delta\widehat{H} = \int_{278\text{ K}}^{300\text{ K}} C_{P,\text{solid}}\,dT + \Delta\widehat{H}_{\text{fus}} + \int_{300\text{ K}}^{350\text{ K}} C_{P,\text{liquid}}\,dT + \Delta\widehat{H}_{\text{vap}}$$

$$+ \int_{350\text{ K}}^{T} C_{P,\text{gas}}^{*}\,dT$$

$$815\,\frac{\text{kJ}}{\text{kg}} = \int_{278\text{ K}}^{300\text{ K}} \left(3\,\frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right) dT + 175\,\frac{\text{kJ}}{\text{kg}} + \int_{300\text{ K}}^{350\text{ K}} \left(3.6\,\frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right) dT + 300\,\frac{\text{kJ}}{\text{kg}}$$

$$+ \int_{350\text{ K}}^{T} (4186.8 - 6.28T + (13.56\times10^{-3})T^{2})\,dT$$

$$94\,\frac{\text{kJ}}{\text{kg}} = \int_{350\text{ K}}^{T} (4186.8 - 6.28T + (13.56\times10^{-3})T^{2})\,dT$$

Solving manually, or by numerical solution software:

$$T = 375\text{ K}$$

2-26. The compound is initially at 370 K. If the pressure is constant at $P = 101.325$ kPa throughout the process, and the specific internal energy of the compound is decreased by 350 kJ/kg, what is the final temperature?

Solution:

Start by determining how much change in specific internal energy occurs when the compound is cooled from 370 K to 350 K (we can call this process A). Assuming ideal gas behavior:

$$\Delta\widehat{U}_{\text{A}} = \int_{T_1}^{T_2} C_V^{*}\,dT = \int_{T_1}^{T_2} (C_P^{*} - R)\,dT$$

$$\Delta\widehat{U}_{\text{A}} = \int_{370\text{ K}}^{350\text{ K}} 4186.8 - 6.28T + (13.56\times10^{-3})T^{2}$$

$$- \left(8.314\,\frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}\right)\left(20\,\frac{\text{mol}}{\text{kg}}\right)\left(\frac{\text{J}}{\text{Pa}\cdot\text{m}^3}\right)\,dT$$

$$\Delta\widehat{U}_{\text{A}} = -73.68\,\frac{\text{kJ}}{\text{kg}} - 3.33\,\frac{\text{kJ}}{\text{kg}} = -77.01\,\frac{\text{kJ}}{\text{kg}}$$

The change in internal energy for vaporization is 241.8 kJ/kg (see solution to problem 2.23). Condensation is the reverse process so it has a change in specific internal energy of –241.8 kJ/kg. Consequently the change in specific internal energy to go from the initial state to saturated liquid at 350 K is $\Delta\widehat{U} = -77.01 - 241.8 = -318.81\,\frac{\text{kJ}}{\text{kg}}$..

Since the total change in specific internal energy is –350 kJ/kg, we can determine the final temperature as:

$$\Delta \hat{U} = \Delta \hat{U}_A + \Delta \hat{U}_B + \Delta \hat{U}_C$$

$$-350 \frac{kJ}{kg} = -77.01 - 241.8 + \int_{350\,K}^{T} C_{P,\text{liquid}}\, dT$$

$$-350 \frac{kJ}{kg} = -77.01 - 241.8 + \int_{350\,K}^{T} \left(3.6 \frac{kJ}{kg \cdot K}\right) dT$$

T = 341.3 K

2-27. This question involves using the steam tables in Appendix A, but answer questions A-C before looking at the steam tables.

A. The density of liquid water at ambient conditions is about 1 g/cm^3. Convert this into a specific volume, expressed in m^3/kg- the units used in the steam tables.

B. You're asked to look up the largest and smallest values of $\hat{V}$ found anyplace in the steam tables. Recall that Appendix A includes saturated steam tables, superheated steam tables and compressed liquid tables, and that the conditions in the tables range from 0.01-100 MPa and 273.15 K-1273.15 K. Where will you look for the largest and smallest values?

C. Before looking up the largest and smallest values of $\hat{V}$, guess or estimate what they will be.

D. Look up the largest and smallest values of $\hat{V}$ found anyplace in the steam tables. How do they compare to the guess/estimates you made in part C? Are they located in the place you predicted in part B?

Solution:

A. The inverse of density is specific volume

$$\frac{1}{\left(1\frac{g}{cm^3}\right)\left(100\frac{cm}{m}\right)\left(100\frac{cm}{m}\right)\left(100\frac{cm}{m}\right)\left(\frac{1}{1000}\frac{kg}{g}\right)} = 0.001\frac{m^3}{kg}$$

B. The largest value of specific volume would be found at the lowest pressure and the highest temperature for superheated steam. The smallest specific volume would be compressed liquid at high pressures and low temperatures

C. Since liquid is close to incompressible, a good guess for liquid would be slightly smaller than the specific volume at ambient conditions. The answer turns out to be around $0.00095 \frac{m^3}{kg}$ but anything slightly smaller than $0.001 \frac{m^3}{kg}$ would be a reasonable guess based on what we know before scanning the tables.

Steam is able to expand, especially in a vacuum with a high temperature. One reasonable way to guess the highest specific volume would be to take the highest T (1273.15 K) and the lowest P (which is 0.01 MPa in the *superheated* steam tables) and plug them into the ideal gas law, giving an answer very close to the 58.7578 $\frac{m^3}{kg}$ found in the superheated steam tables.

However, the "Saturation temperature" table contains data on saturated steam at 273.15 K, which corresponds to a vapor pressure of only 0.00061 MPa, and this has the largest specific volume anywhere in these tables. Even higher specific volumes could be obtained if the tables were expanded to include superheated steam at these extremely low pressures.

D. Steam at 1273.15 K and 0.01 MPa → 58.7578 $\frac{m^3}{kg}$

But saturated steam at 273.15 K°C and 0.00061 MPa → 206.13 $\frac{m^3}{kg}$

Water at 273.15 K and 100 MPa → 0.000957$\frac{m^3}{kg}$

2-28. Model water using the van der Waals equation of state with $a= 5.53 \times 10^6$ bar·cm^6/mol^2 and $b=30.48$ cm^3/mol.

A. Make a graph of P vs. $\hat{V}$ for water at $T=100$°C, using data from the steam tables.
B. Using the van der Waals equation of state, plot a graph of P vs. $\hat{V}$ for water, holding temperature constant at $T=100$°C. Compare this to the data from part A and comment on the quality of the predictions produced by the van der Waals equation.
C. Repeat parts A and B for temperatures of 200°C, 300°C, 400°C and 500°C. When you compare the five temperatures to each other, what differences in behavior do you notice, for both the real data and the equation of state?

Solution:

A. A sample calculation at 100°C follows:

The data in the steam tables was converted from m^3/kg into cm^3/mol for consistency with the given units of a and b. Thus, from steam tables, at P=1 bar, $\hat{V}$ =1.6959 m^3/kg.

$$\left(1.6959 \ \frac{m^3}{kg}\right)\left(\frac{100 \ cm}{m}\right)^3 \left(\frac{1 \ kg}{1000 \ g}\right)\left(\frac{18.02 \ g}{mol}\right) = 30,560 \ \frac{cm^3}{mol}$$

This process can be repeated for all of the data points in the steam tables. This same volume is used for the sample calculation in part B.
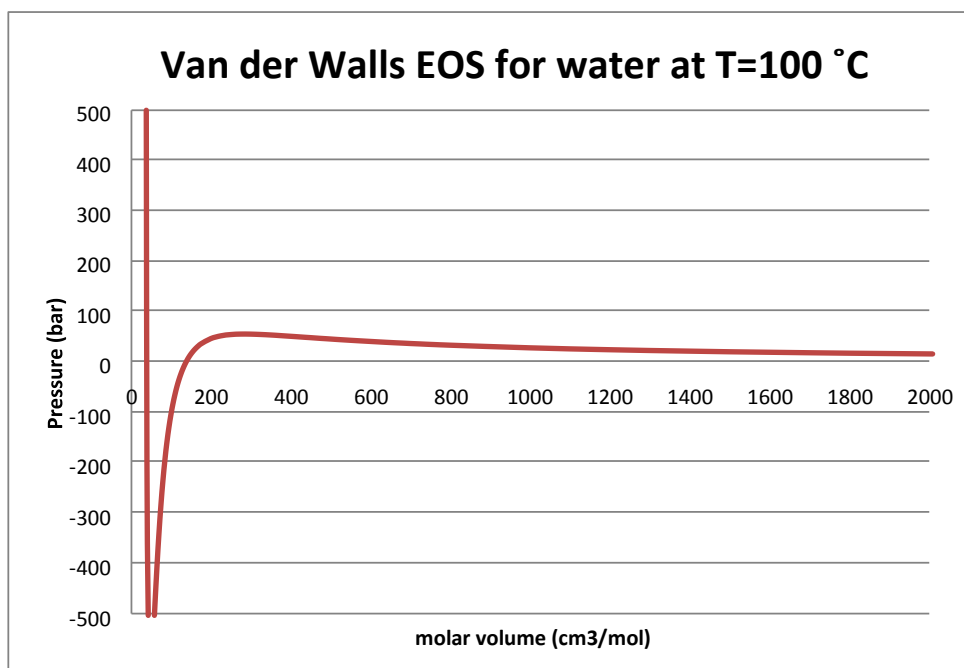
B. The Van der Waals EOS is:

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

Thus when V = 30,560 cm^3/mol:

$$P = \frac{\left(83.14 \frac{cm^3}{mol}\right)(373.15 \ K)}{30{,}560 - 30.48 \ \frac{cm^3}{mol}} - \frac{5.535 \times 10^6 \ \frac{bar\,cm^6}{mol^2}}{\left(30{,}560 \ \frac{cm^3}{mol}\right)^2} = \ 1.025 \ bar$$

Using a spreadsheet, a full plot of P vs. V from the VDW equation can be constructed and plotted, like the following:

As explained in Example 2-6, VDW is a cubic equation and there can be as many as three distinct values of $\underline{V}$ that produce the same P. In such a case, we might interpret the largest $\underline{V}$ as the vapor value and the smallest $\underline{V}$ as the liquid value. This is discussed further in Section 7.2.4.

C. The most straightforward way to do a comparison is to construct one or more plots that contain both the data from the steam tables and the VDW calculations from part B.

However care must be taken to construct the plots in a way that enables fair comparisons. For example a plot like this one would suggest the agreement is outstanding:
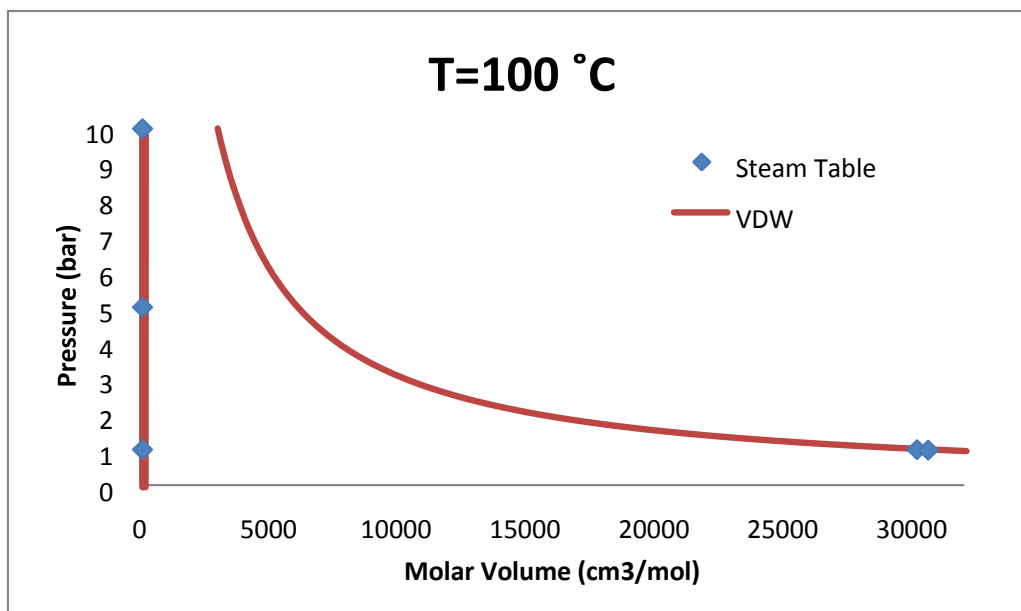
And the agreement is indeed very good for the vapor phase at this temperature. However the liquid phase predictions are not at all good as illustrated by this plot:
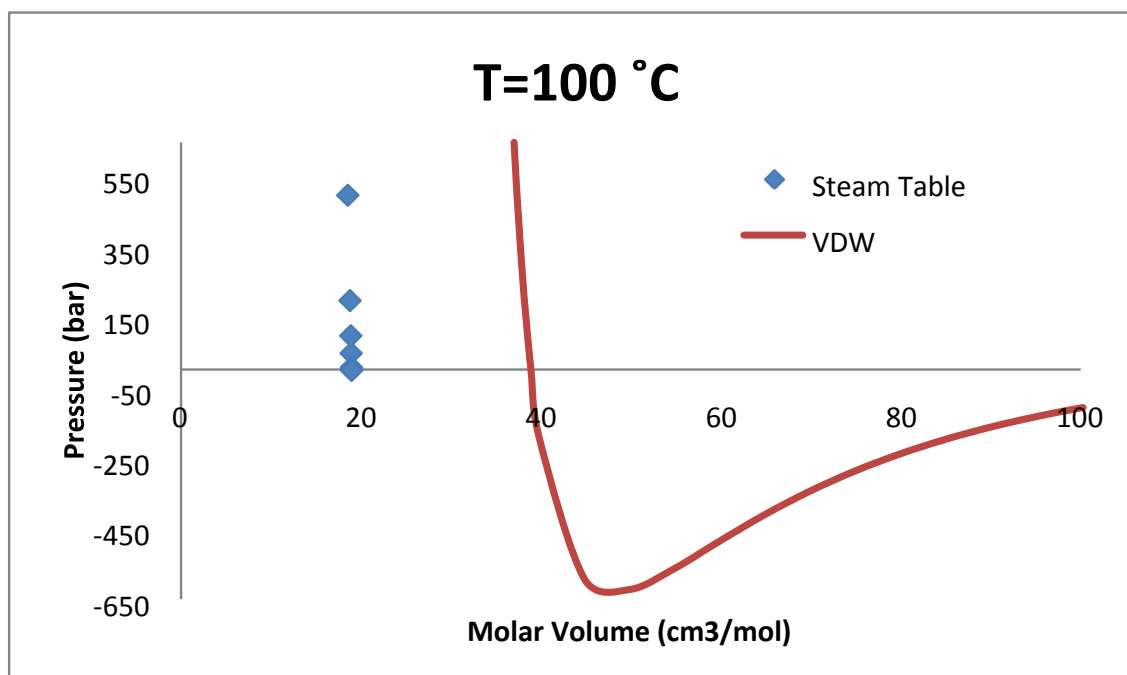

This plot shows that the VDW equation predicts liquid molar volumes in the range of 3839 cm^3/mol for pressures of 5-500 bar. If you insert the actual liquid molar volumes (~18 cm^3/mol) into the VDW equation, you get a negative pressure, because $\underline{V}<b$.

The above perhaps suggests that the value of "b" given in the problem statement must be wrong. Since the whole intent of the parameter "b" (as described in section 2.3.4) is to

represent the "minimum possible molar volume" of the compound, it makes no sense that the experimentally measured $\underline{V}$ would be smaller than b. But the values of a and b given in this problem statement are indeed the "correct" ones for water, according to a technique that will be illustrated in Section 7.2.5. The problem is not the values of a and b themselves, the problem is that the van der Waals EOS isn't robust enough to model both liquid and vapor molar volumes.

At T=200°C the vapor pressure of water is over 15 bar, and at 300°C it is over 85 bar, so much more vapor-phase data is available. The agreement is again good for the vapor phase (though departures become more noticeable as pressure increases) but very poor for the liquid phase.

T=200 ˚C
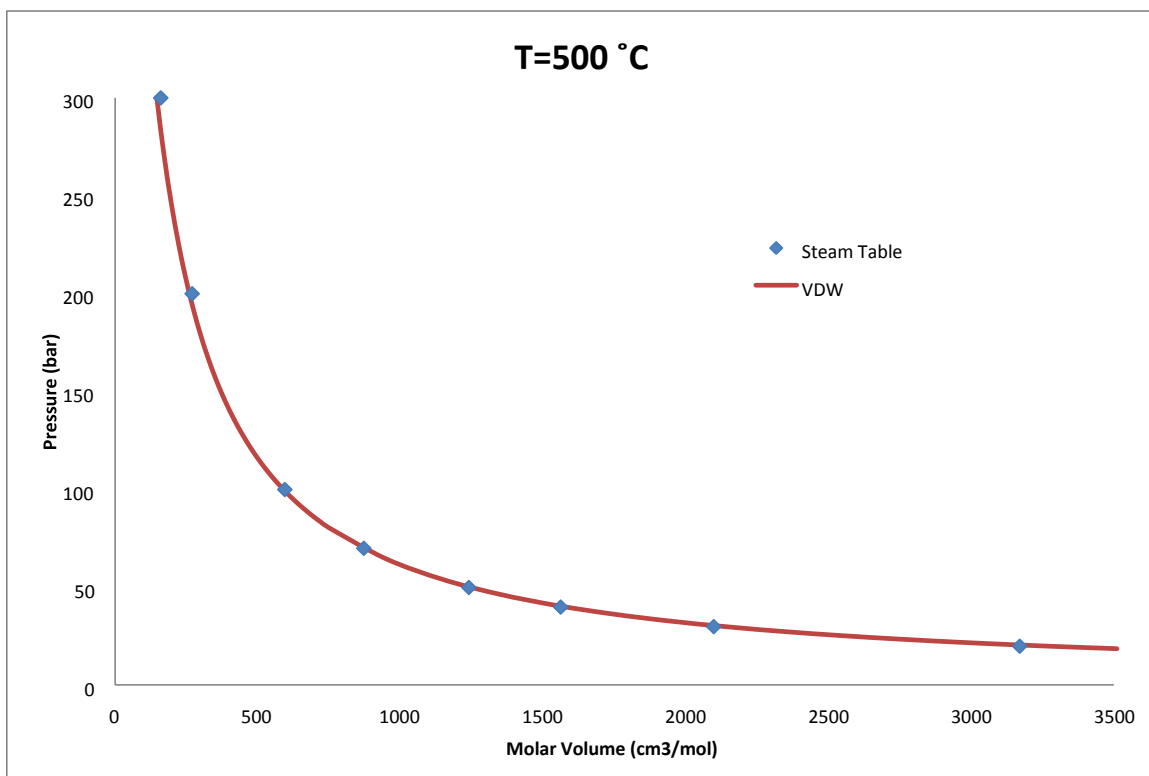

T=300 ˚C

T=300 ˚C
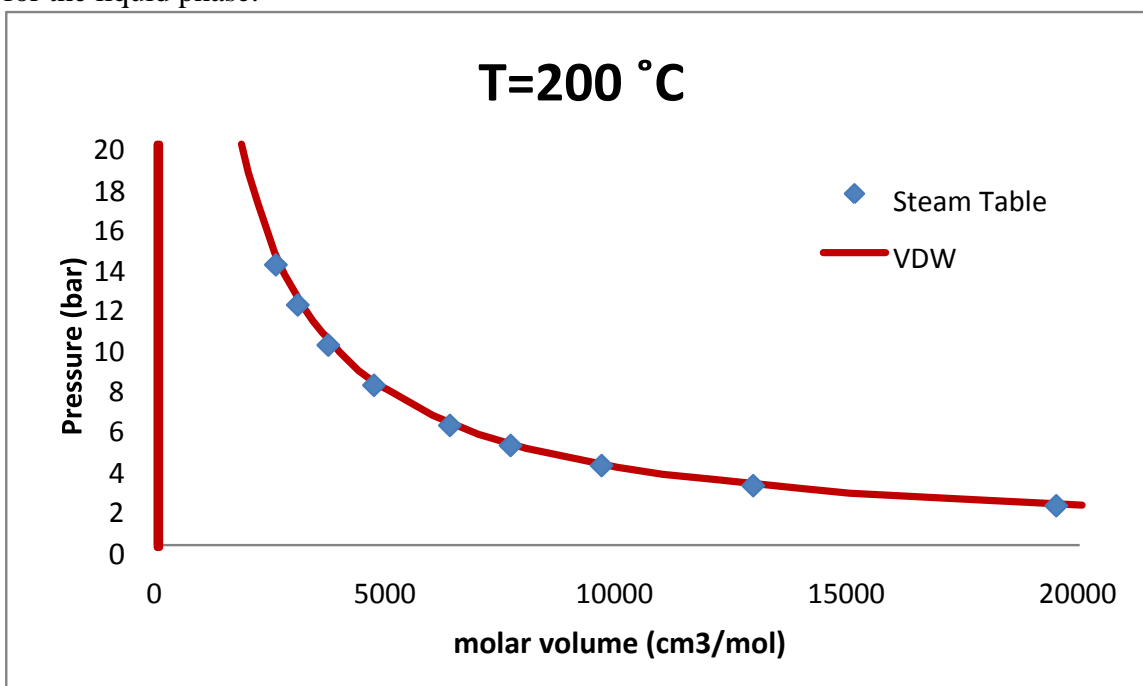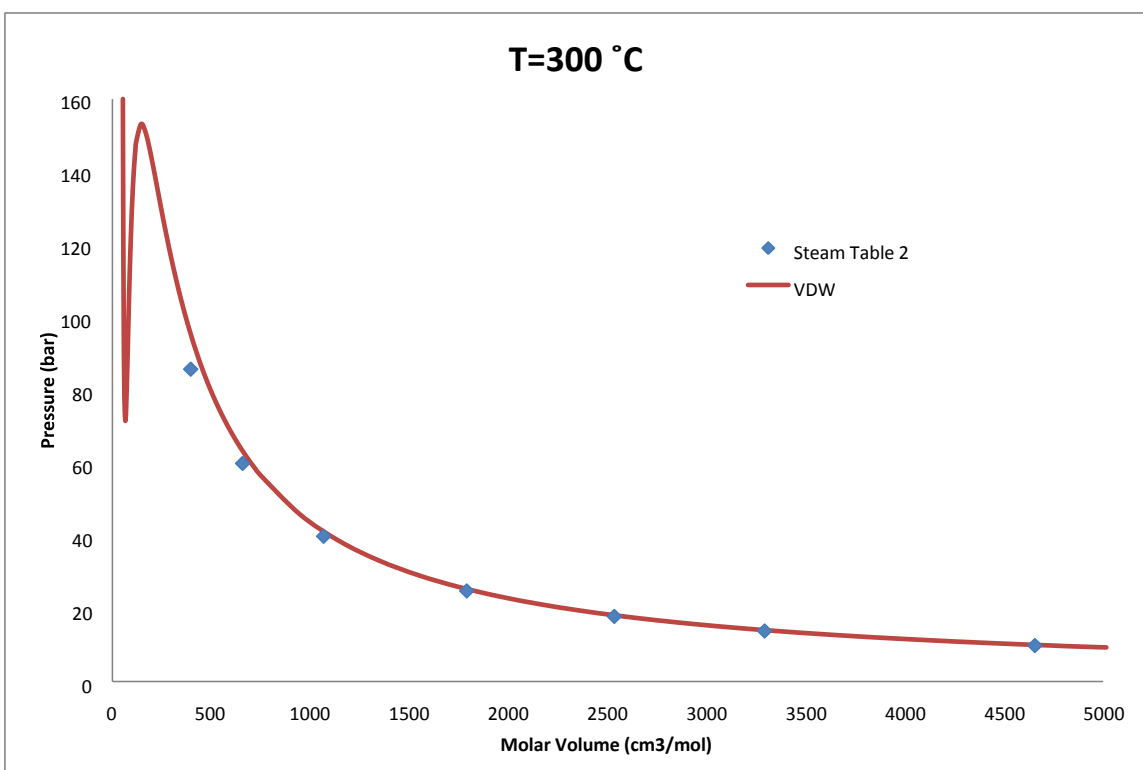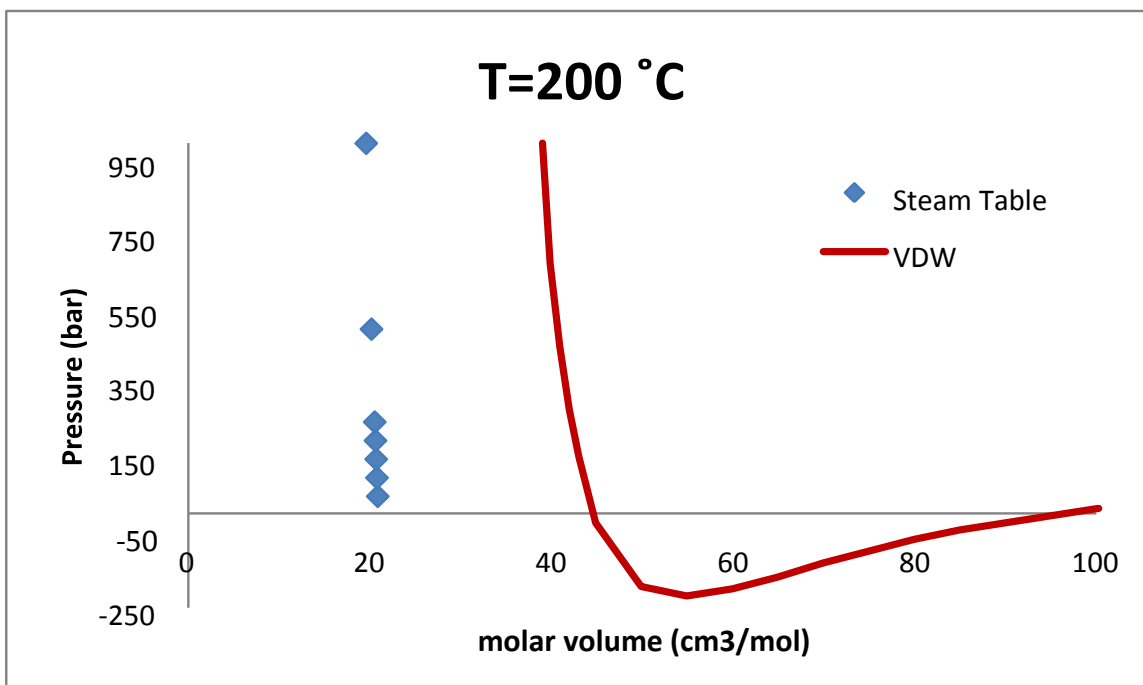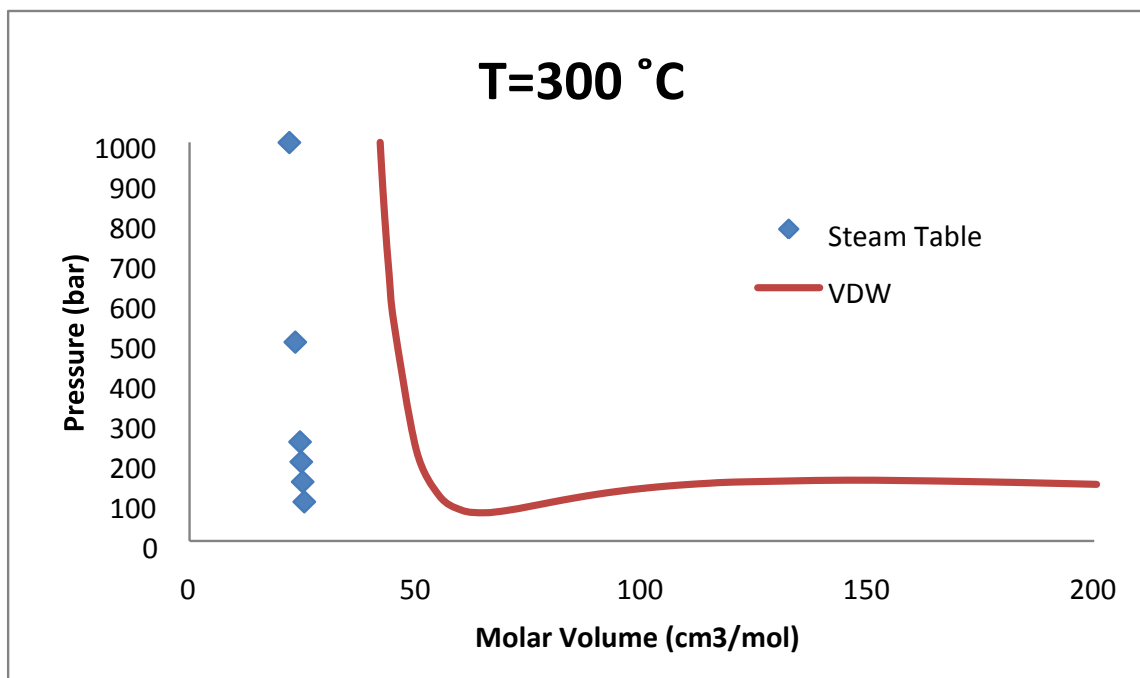
400 and 500°C are above the critical point so the complication of two phases is no longer present in the data at these temperatures. Also, the van der Waals equation P vs. $\underline{V}$ plot no longer has maxima or minima at these temperatures; the volume simply decreases with increasing pressure. This, too, is explained further in Section 7.2.5.

T=400 ˚C
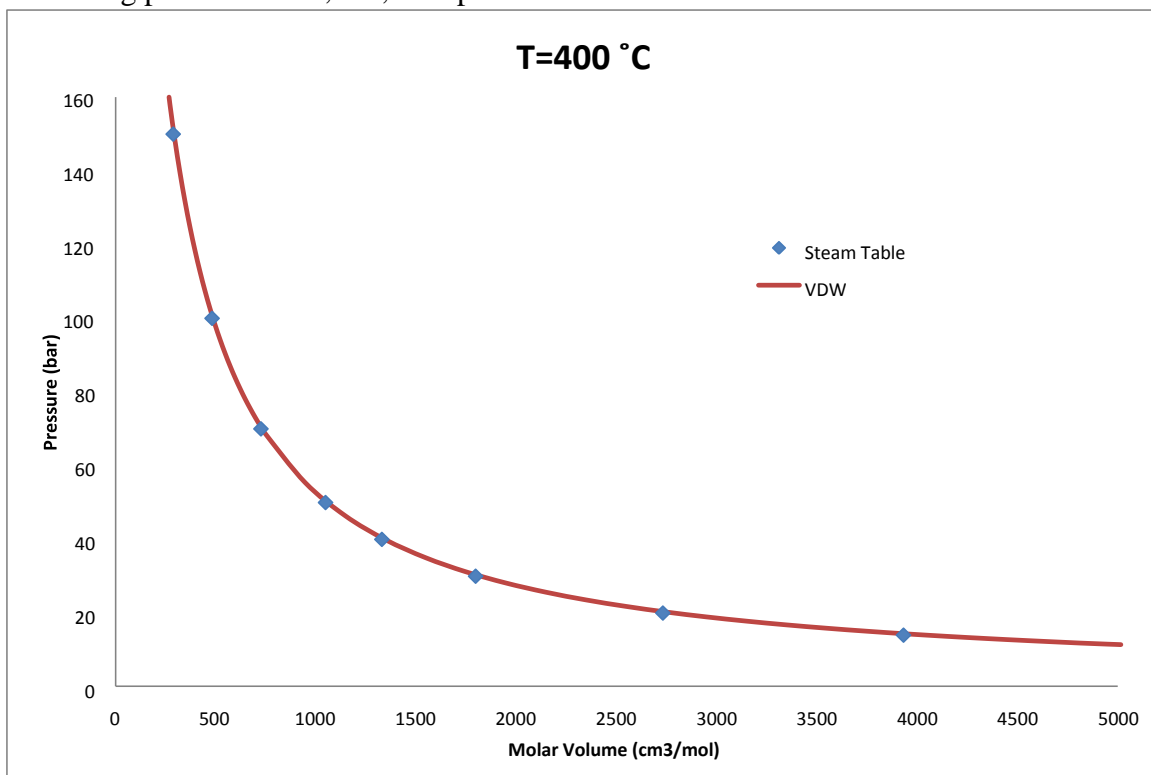
2-29. A compound has a molecular mass of 120 kg/kmol, and the information in the table below is the only other data available for a compound. Fill in all of the empty cells with your best estimate of the value. Explain any assumptions or approximations you make.

The completed table is below, with given information in regular type, and answers in bold. Explanations for each individual question follow.

	Phase	**T (K)**	**P (MPa)**	**$\hat{U}$ (kJ/kg)**	**$\hat{H}$ (kJ/kg)**	**$\hat{V}$ (m³/kg)**
A	Solid	273	0.5	–42.6	**–42.2**	8.0×10^{-4}
B	Solid	298	0.5	0	**0.4**	$\mathbf{8.0 \times 10^{-4}}$
C	Liquid	298	0.5	63.0	63.6	**0.0012**
D	Liquid	333	0.5	**156.1**	**156.7**	**0.0012**
E	Liquid	358	0.5	**222.6**	223.2	**0.0012**
F	Vapor	358	0.5	977.2	1014.2	**0.074**
G	Vapor	358	0.1	961.2	**986.0**	**0.248**

Chapter 2: The Physical Properties of Pure Compounds

A. Apply definition H=U+PV

$$\hat{H} = \hat{U} + P\hat{V} = \left(-42.6 \; \frac{kJ}{kg}\right) + (0.5 \; MPa)\left(8 \times 10^{-4} \; \frac{m^3}{kg}\right)\left(\frac{N}{Pa \cdot m^2}\right)\left(\frac{J}{N \cdot m}\right)$$

$$= -42.2 \; \frac{kJ}{kg}$$

B. Assume $\hat{V}$~constant for solid over 25 K temperature interval. Compute $\hat{H}$ as in part A.

C. Apply definition H=U+PV

$$\hat{V} = \frac{\hat{H} - \hat{U}}{P} = \left(\frac{63.6\frac{kJ}{kg} - 63.0 \; \frac{kJ}{kg}}{0.5 \; MPa}\right)\left(\frac{N}{Pa \cdot m^2}\right)\left(\frac{J}{N \cdot m}\right)$$

$$\hat{V} = 0.0012 \; \frac{m^3}{kg}$$

Assume this value also applies to parts D and E since there is no information that would allow us to estimate expansion with temperature.

D. Assume the liquid heat capacity C_P is constant. Use known values from C and E to estimate what it is:

$$d\hat{H} = C_P dT$$

For constant C_P this integrates to:

$$\hat{H}_2 - \hat{H}_1 = C_P(T_2 - T_1)$$
$$\left(223.2\frac{kJ}{kg} - 63.6 \; \frac{kJ}{kg}\right) = C_P(358 \; K - 298 \; K)$$
$$C_P = 2.66 \; \frac{kJ}{kg}$$

Use to find unknown specific enthalpy at 60°C:

$$\hat{H}_2 - \hat{H}_1 = C_P(T_2 - T_1)$$

$$\left(223.2\frac{kJ}{kg} - \hat{H}_1\right) = \left(2.66 \; \frac{kJ}{kg}\right)(358 \; K - 333 \; K)$$

$$\hat{H}_1 = 156.7 \; \frac{kJ}{kg}$$

Apply definition H=U+PV to find specific internal energy:

$$\hat{U} = \hat{H} - P\hat{V} = \left(156.7 \, \frac{kJ}{kg}\right) - (0.5 \, \text{MPa})\left(0.0012 \, \frac{m^3}{kg}\right)\left(\frac{N}{Pa \cdot m^2}\right)\left(\frac{J}{N \cdot m}\right)$$

$$= 156.1 \, \frac{kJ}{kg}$$

E. Find $\hat{U}$ as in part D

F. Find $\hat{V}$ as in part C

G. Low pressure, estimate volume using ideal gas law:

$$\underline{V} = \frac{RT}{P} = \frac{\left(8.314 \, \frac{Pa \cdot m^3}{mol \cdot K}\right)(358 \, K)}{(0.1 \, \text{MPa})} = 0.02978 \, \frac{m^3}{mol}$$

$$\hat{V} = \left(0.02978 \, \frac{m^3}{mol}\right)\left(\frac{1 \, \text{kmol}}{120 \, kg}\right)\left(1000 \, \frac{mol}{kmol}\right) = 0.248 \, \frac{m^3}{kg}$$

Then find $\hat{U}$ as in part A.

Chapter 2: The Physical Properties of Pure Compounds