Assignment #8 - Solutions

Individual Exercises:

1. Consider the \( \overline{G}_p(T) \) and \( \overline{G}_T(P) \) plots shown in M&S Figs. 9.10 and 9.11. What restrictions, if any, apply to the slopes and curvatures of such plots?

The slopes on these plots are the first derivatives of \( \overline{G} \),

\[
\left( \frac{\partial \overline{G}}{\partial T} \right)_P = -\overline{S} \leq 0 \quad \left( \frac{\partial \overline{G}}{\partial P} \right)_T = +\overline{V} \geq 0
\]

(These inequalities are required by the positivity of entropy, ensured by the 3rd Law, and of volume, which is positive by definition.) The curvatures are the second derivatives:

\[
\left( \frac{\partial^2 \overline{G}}{\partial T^2} \right)_P = -\left( \frac{\partial \overline{S}}{\partial T} \right)_P = -\frac{\overline{C}_p}{T} \leq 0 \quad \left( \frac{\partial^2 \overline{G}}{\partial P^2} \right)_T = +\left( \frac{\partial \overline{V}}{\partial P} \right)_T = -\overline{\kappa}_T \leq 0
\]

The requirement that both of these 2nd derivatives be negative derives from the conditions of thermal \( (\overline{C}_p \geq 0) \) and mechanical stability \( (\kappa_T \geq 0) \).

2. Use the “steam chart” from the Topic 9 handout to estimate the following:
   (a) the mole fraction of liquid water in a 500 L drum containing 5 kg of saturated steam at 150 °C.
   (b) the work done and the heat released when steam is compressed isothermally and reversibly at 200 °C between pressures of 0.1 bar and 100 bar.

(a) The specific volume corresponding to these conditions is 0.1 m\(^3\) kg\(^{-1}\). Measuring the distance between the coexistence lines as illustrated in red on the chart shown below, I used the “lever rule” to estimate the liquid and vapor mole fractions to be:

\[
x_L = \frac{L_2}{L_1 + L_2} \approx \frac{5.1}{1.7 + 5.1} = 0.75 \quad \text{and} \quad x_V = 1 - x_L \approx 0.25
\]

(b) The process described corresponds to the path #1→#2 shown in green on the chart below. Since the process is reversible and isothermal the heat involved can be calculated from
\[ \dot{q}_{\text{rev}} = \int_{1}^{2} Td\dot{S} = T(\dot{S}_2 - \dot{S}_1) \]

The caret on these symbols denotes the fact that I’m doing the calculation for 1 kg of water. (I forgot to state the quantity on the problem, so I’ll report the results on this basis.) Reading the values of entropy from the chart, I estimate:

\[ \dot{q} = (473.15 \text{ K})(2.3 - 8.9 \text{ kJ K}^{-1} \text{ kg}^{-1}) = -3.1 \text{ MJ/kg} \]

(Since \( q \) is negative the system gives off heat, as expected in an isothermal compression.)

Determining the work required requires a little more work (pun intended):

\[ \dot{w}_{\text{rev}} = \Delta \hat{U} - \dot{q}_{\text{rev}} = \Delta \hat{H} - \Delta (P\hat{V}) - \dot{q}_{\text{rev}} \]

All of the pieces can be read from the diagram as follows:

\[ \Delta \hat{H} = 0.86 - 2.88 \text{ MJ/kg} = -2.02 \text{ MJ/kg} \]
\[ \Delta (P\hat{V}) = P_2 \hat{V}_2 - P_1 \hat{V}_1 = (10^7 \times 1.1 \times 10^{-3} - 10^4 \times 30 \text{ Pa m}^3 \text{ kg}^{-1}) = -0.29 \text{ MJ/kg} \]

so \[ \dot{w}_{\text{rev}} = +0.79 \text{ MJ/kg} \]

The work is positive as it must be for a compression. (Note the relatively small (~10%) difference that the \( PV \) term makes compared to the “thermal” terms – i.e. the relatively small difference between \( \Delta \hat{H} \) and \( \Delta \hat{U} \).)
3. (a) What is the relationship between chemical potential and fugacity?
(b) M&S 9-38: Show that Eqs. 9.30 and 9.32 for \( \mu(T, P) \) for a monatomic ideal gas are equivalent to using the relation \( G = H - TS \) with \( H = \frac{1}{2} RT \) and \( S \) given by Eq. 6.45.

(a) Fugacity can be defined:

\[
f = P \exp \left( \frac{G - G^{IG}}{RT} \right)
\]

Since the chemical potential is the same as the molar Gibbs energy for a pure substance the relationship is simply

\[
f = P \exp \left( \frac{H - H^{IG}}{RT} \right)
\]

(b) I will ignore the route suggested by the problem and demonstrate the relationship between \( S, H, \) and \( \mu \) in Eq. 9.29 in a different (and in my opinion more logical) way. Eq. 6-45 derives from the general relation:

\[
S = k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} + k_B \ln Q
\]

Similarly, the relationship between the internal energy and \( Q \) is:

\[
U = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}
\]

Using these two expressions, \( G \) can be written in terms of \( Q \) via:

\[
G = H - TS
= U - TS + PV
= U - TS + Nk_B T
= -k_B T \ln Q + Nk_B T
\]

where the use of \( PV = Nk_B T \) specializes these expressions for ideal gas problems.

For a partition function of the ideal gas form, \( Q(N, V, T) = q(V, T)^N / N! \), \( G \) can be rewritten as
\[ G = -(Nk_B T \ln q - k_B T \ln N!) + Nk_B T \]
\[ = -(Nk_B T \ln q - Nk_B T \ln N + Nk_B T) + Nk_B T \]
\[ = -Nk_B T \ln \frac{q}{N} \]

(The 2nd of these equations makes use of Stirling’s approximation \( \ln N! \approx N \ln N - N \).

Considering 1 mole of gas, \( N \rightarrow N_A \), \( G \rightarrow \bar{G} = \mu \), and \( N_A k_B = R \), so that this expression transforms into:

\[ \mu = -RT \ln \frac{q(V, T)}{N_A} = -RT \ln \left[ \frac{q(V, T)}{V} \frac{V}{N_A} \right] = -RT \ln \left( \frac{q(V, T)}{V} \right) \cdot \frac{V}{N_A} \].

4. (a) M&S 9-4: The vapor pressures of solid and liquid chlorine are given by
\[ \ln(P_S / \text{torr}) = 24.320 - 3777 K / T \]
\[ \ln(P_L / \text{torr}) = 17.892 - 2669 K / T \]
where \( T \) is the absolute temperature. Calculate the temperature and pressure at the triple point of chlorine.

(b) M&S 9-6: The slope of the melting curve of methane is given by:
\[ \frac{dP}{dT} = (0.08446 \text{bar} \cdot K^{-1.85}) T^{0.85} \]
from the triple point to arbitrary temperatures. Using the fact that the temperature and pressure at the triple point are 90.68 K and 0.1174 bar, calculate the melting pressure of methane at 300 K.

Equilibrium between the liquid and solid requires equal vapor pressures (i.e. the pressures of all three phases must be equal). Equating the two expressions for \( \ln(P) \) and solving for temperature one finds:
\[ 24.320 - 3777 K / T = 17.892 - 2669 K / T \]
\[ T_p / K = \frac{3777 - 2669}{24.320 - 17.892} = 172.4 \]

The pressure is given by inserting this temperature into either equation:
\[ P_p / \text{torr} = \exp \left( \frac{24.320 - 3777}{172.37} \right) = 11.1 \]

(b) For a relationship of the form \( (dP / dT) = aT^\alpha \) the pressure at any temperature can be determined given data at some reference \((T, P)\) point via:
\[ P(T) = P(T_0) + \int_{T_0}^{T} aT^\alpha dT' = P(T_0) + \frac{a}{\alpha + 1} [T^{\alpha + 1} - T_0^{\alpha + 1}] \]

I actually performed the evaluation of this integral in Mathcad using the triple point data for reference with the result:

\[
\begin{align*}
\text{bar} &:= 10^5 \cdot \text{Pa} & T_{tp} &:= 90.68 \cdot \text{K} & P_{tp} &:= 0.1174 \cdot \text{bar} & a &:= 0.08446 \cdot \text{bar} \cdot \text{K}^{-1.85} \\
P(T) &:= P_{tp} + \int_{T_{tp}}^{T} a \cdot x^{0.85} \, dx & P(300 \cdot \text{K}) &= 1.556 \times 10^3 \\
\end{align*}
\]

5. Nearly all boiling and melting points in the literature are reported as the normal (1 atm) values. The difference between the normal and standard melting points of a substance is completely negligible (Why?). However, the difference between the normal and standard boiling points, although small, may not be negligible for some purposes.

(a) Using the same approximations that led to Eq. 9.12 in the text, derive the expression:

\[
\frac{\Delta T_b}{T_b} \simeq \frac{R}{\Delta_{vap}S} \frac{\Delta P}{P}
\]

(b) Use this expression and Trouton’s rule to obtain an approximate numerical estimate of \( \Delta T_b / T_b \equiv (T_{nb} - T_{sb}) / T_{nb} \), the relative difference in the normal and standard boiling points, applicable to all substances (at least to within the approximations specified).

(c) Estimate the standard boiling points of H_2O, CCl_4, and benzene using the data tabulated in the Topic 9 handout. Compare your results to the accurate values of 372.77, 349.34, and 352.89 K determined for these liquids.

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(a) The (exact) Clapeyron equation is:

\[
\frac{dT}{dP}_{vap} \equiv \frac{\Delta_{vap}V}{\Delta_{vap}S}
\]

Neglecting the volume of the liquid compared to the volume of the vapor, \( \Delta_{vap}V \simeq V' \). Assuming the vapor to be an ideal gas, \( \Delta_{vap}V \simeq RT / P \), this equation becomes

\[
\frac{dT}{dP}_{vap} \simeq \frac{R}{\Delta_{vap}S} \frac{T}{P} \quad \text{or} \quad \frac{dT}{T} \simeq \frac{R}{\Delta_{vap}S} \frac{dP}{P}
\]

(Although not explicitly subscripted “vap”, \( T \) and \( P \) refer to values under liquid – vapor coexistence conditions.) For pressures of 1 atm or 1 bar the vaporization transition is referred
to as “boiling” so \( T \rightarrow T_b \). For a difference as small as that between 1 atm and 1 bar, \( dP \cong \Delta P \) so that one finally obtains the desired result:

\[
\frac{\Delta T_b}{T_b} \cong \frac{R}{\Delta_{vap}S} \frac{\Delta P}{P}
\]

(b) Trouton’s rule states that the entropy of vaporization at the (normal) boiling point is approximately 10.5 R. Thus,

\[
\frac{\Delta T_b}{T_b} \equiv \frac{T_{nb} - T_{sb}}{T_{nb}} \cong \frac{R}{\Delta_{vap}S} \frac{P_{nb} - P_{sb}}{P_{nb}} \cong \frac{1}{10.5} \frac{(1 \text{ atm} - 1 \text{ bar})}{1 \text{ atm}} = 1.24 \times 10^{-3}
\]

Within the approximations made above the fractional difference between the normal and standard boiling points is a constant.

(c) The standard boiling points can be estimated from

\[
T_{sb} = T_{nb} \left(1 - \frac{\Delta T_b}{T_b}\right)
\]

with \( \Delta T_b / T_b \) either estimated using the universal value of \( 1.24 \times 10^{-3} \) (“#1” in the table below) or the more accurate expression \( \Delta T_b / T_b \cong (R / \Delta_{vap}S) \times 0.01308 \), which does not employ Trouton’s rule (“#2” below). I used an Excel spreadsheet to carry out both calculations with the results tabulated below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta_{vap}S ) /R</th>
<th>( T_{nb} ) /K</th>
<th>( \Delta T_b ) #1 /K</th>
<th>( \Delta T_b ) #2 /K</th>
<th>( T_{sb} ) #1 /K</th>
<th>( T_{sb} ) #2 /K</th>
<th>( T_{sb} ) - Exp. /K</th>
<th>Err #1 /%</th>
<th>Err #2 /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>13.11</td>
<td>373.15</td>
<td>-0.463</td>
<td>-0.372</td>
<td>372.69</td>
<td>372.77</td>
<td>-22%</td>
<td>2.0%</td>
<td></td>
</tr>
<tr>
<td>CCl4</td>
<td>10.31</td>
<td>349.77</td>
<td>-0.434</td>
<td>-0.444</td>
<td>349.34</td>
<td>349.33</td>
<td>-0.9%</td>
<td>-3.2%</td>
<td></td>
</tr>
<tr>
<td>C6H6</td>
<td>10.47</td>
<td>353.32</td>
<td>-0.438</td>
<td>-0.441</td>
<td>352.88</td>
<td>352.88</td>
<td>-1.9%</td>
<td>-2.7%</td>
<td></td>
</tr>
</tbody>
</table>

The errors listed in this table are the % errors in the difference \( \Delta T_b \) rather than in the temperatures themselves. (The % error in the latter values would, of course be much smaller.) Only in the case of water is there a substantial error in the simple (method #1) estimate. In all cases the method #2 estimate provides \( \Delta T_b \) to within a few percent.

5. M&S 9-22 with modifications. The vapor pressure of mercury from 400 °C to from 1300 °C can be expressed by:

\[
\ln(P / \text{torr}) = 17.85 - \frac{7060.7 \text{ K}}{T}
\]

The density of the vapor at its normal boiling point is 3.82 g L\(^{-1}\) and that of the liquid is 12.7 g mL\(^{-1}\). Estimate the molar enthalpy of vaporization of mercury at its normal boiling point.
(a) First solve this problem using the exact relation between \( \frac{dP}{dT} \) \(_{\text{vap}}\) and \( \Delta_{\text{vap}}H \).

(b) Solve this problem again using the more approximate Clausius-Clapeyron relation.

(c) Calculate the % error in the estimate of part (b) and identify the largest source of error in this approximation.

The exact relationship between the slope of the coexistence curve and \( \Delta_{\text{vap}}H \) is:

\[
\left( \frac{dP}{dT} \right)_{\text{vap}} = \frac{\Delta_{\text{vap}}H}{T_{\text{vap}} \Delta_{\text{vap}}V} \quad \text{or} \quad \Delta_{\text{vap}}H = \left( \frac{dP}{dT} \right)_{\text{vap}} T_{\text{vap}} \Delta_{\text{vap}}V
\]

The vapor pressure equation can be expressed in the form \( P / \text{torr} = \exp(a + b / T) \) which is easily solved for \( T(P) \) and for the slope of the coexistence curve:

\[
T(P) = \frac{b}{\ln(P / \text{torr}) - a} \quad \frac{dP}{dT} / \text{torr} = -\frac{b}{T^2} \exp(a + b / T)
\]

(I’ve kept the units on \( P \) as a reminder that they are not SI units and will need to be converted for use in the Clapeyron equation.)

Finally \( \Delta_{\text{vap}}V \) is given by:

\[
\Delta_{\text{vap}}V = M \left( \frac{1}{\rho^V} - \frac{1}{\rho^L} \right)
\]

Using these equations in the Mathcad worksheet shown on the following page provides the result:

\[
\Delta_{\text{vap}}H = 59.66 \text{ kJ/mol}
\]

(b) The Clausius-Clapeyron equation can be written:

\[
\left( \frac{d \ln P}{dT} \right)_{\text{vap}} \cong \frac{\Delta_{\text{vap}}H}{RT_{\text{vap}}^2} \quad \text{or} \quad \Delta_{\text{vap}}H \cong RT_{\text{vap}}^2 \left( \frac{d \ln P}{dT} \right)_{\text{vap}}
\]

For the form of the vapor pressure curve provided, \( (d \ln P / dT) = b / T^2 \) and one has the simple result:

\[
\Delta_{\text{vap}}H \cong -Rb = 58.70 \text{ kJ/mol}
\]

(c) The error in use of the approximate Clausius-Clapeyron equation is \( -1.6\% \). Given the relative simplicity of the use of this approximate equation, the error is small. There are only two possible sources for this error: i) neglect of the volume of the liquid or ii) the assumption
that the vapor behaves like an ideal gas. As shown by the calculation at the end of the mathcad spreadsheet, nearly all of the error in this case comes from the assumption of ideality.

\[ \%err_2 = 1.637 \]

\[ \%err_1 = 0.03 \]

\[ \Delta H_b = 58.703 \text{ Jmol}^{-1} \]

\[ \Delta V = 0.052 \text{ m}^3/\text{mol} \]

6. **M&S 9-23**: The pressures at the solid-liquid coexistence boundary of propane are given by the empirical equation \( P = -718 + 2.38565T^{1.283} \) where \( P \) is in bar and \( T \) in Kelvin. Given that \( T_{\text{fus}} = 85.46 \text{ K} \) and \( \Delta f_{\text{us}} \bar{H} = 3.53 \text{ kJ mol}^{-1} \), calculate \( \Delta f_{\text{us}} \bar{V} \) at 85.46 K.

Solving the Clapeyron equation for \( \Delta f_{\text{us}} \bar{V} \) provides the relation: 

\[ \frac{\Delta f_{\text{us}} \bar{V}}{T_{\text{fus}} (dP / dT)_{\text{fus}}} = \frac{\Delta f_{\text{us}} \bar{H}}{T_{\text{fus}} (dP / dT)_{\text{fus}}} \]

Carrying out this calculation in Mathcad (worksheet below) yields \( \Delta f_{\text{us}} \bar{V} = 38.3 \text{ cm}^3 \text{ mol}^{-1} \).
Group Problems:

7. (a) M&S 9-10: Plot the following data for the densities of liquid and gaseous ethane in equilibrium with each other as a function of temperature, and determine the critical temperature of ethane.

(b) M&S 9-11: Use the data in the preceding problem to plot \( \frac{\rho_L - \rho_V}{2} \) against \( T - T_c \), with \( T_c = 305.4 \) K. The resulting straight line is an empirical law called the law of rectilinear diameters. If this curve is plotted on the same figure as in the preceding problem, the intersection of the two curves gives the critical density, \( \rho_c \).

(c) A variety of “scaling laws” describe how the properties of a fluid vary as a function of the distance from the critical point. One such law describes the vanishing difference between the coexisting liquid and vapor densities as \( (\rho_L - \rho_v) \rightarrow (T_c - T)\beta \). \( \beta \) in this expression is termed a “critical exponent”. Determine the value of \( \beta \) for ethane using the data provided in M&S 9-10 and assuming that \( T_c = 305.4 \) K.

(a), (b) The plot of coexisting densities is shown below. Using an expanded version of this plot I estimated the critical temperature and density to be those indicated on the plot. The average density versus temperature is indeed a straight line, as expected from the “law” of rectilinear diameters. (As far as I know this law is purely empirical.)

![Graph of coexisting densities](image)

(c) Rather than plot \( T - T_c \) itself, I chose to plot \( \frac{T - T_c}{T_c} \) so as to display the normalized displacement from the critical point. In the log-log representation, these data are close to linear, which means that the power law suggested is a good representation here. I estimated values of \( \beta \) by making linear fits to the data in this representation. Since the scaling behavior that gives rise to this power-law dependence is only expected to be valid close to the critical point, I performed
two fits – one using all of the data and one using only the five points closest to \( T_c \). The results differ slightly. Based on the two fits, I would estimate \( \beta = 0.36 \pm 0.02 \).

8. Assuming that the formation of liquid water is a requirement for ice skating, and that the pressure-dependence of the freezing point of water is the only mechanism for producing the requisite liquid, estimate the lowest temperature (in °C) ice-skating should be possible. Clearly discuss any assumptions and/or approximations you employ.

This problem requires a knowledge of the change of the melting temperature of ice with pressure, which can be obtained in two ways. The simplest and most accurate method is to simply use the graph provided in M&S Fig. 9.6. I read points from this figure in order to obtain the analytic representation:

\[
T_{fus}(P) = 272.7 - 7.55(P/\text{kbar}) - 1.45(P/\text{kbar})^2
\]

The data and fit are plotted at the right. (Note that this expression for \( T_{fus}(P) \) predicts a value of 272.7 K at 1 bar pressure, which is 0.4 K smaller than the correct value of 273.15 K. The discrepancy is simply due to the inaccuracy in reading data from the figure.)

Aside: -------------------------------------------------------------

As an instructive exercise, one can also estimate the required pressure dependence using the Clapeyron equation and the transition properties at 1 atm pressure. The Clapeyron equation can be written in the form:

\[
\frac{dT}{T} = \left( \frac{\Delta V}{\Delta H} \right)_{fus} dP
\]

Making the (poor) approximation that the volume and enthalpy change of fusion (or at least their ratio) is independent of \( P \), this expression integrates to:
\[ T(P) = T(P_0) \exp\{\alpha(P - P_0)\} \quad \text{with} \quad \alpha \equiv \frac{\Delta V}{\Delta H_{\text{fus}}} . \]

In the case of water, \( \Delta_{\text{fus}}V = -1.63 \text{ cm}^3/\text{mol}, \Delta_{\text{fus}}H = 6.01 \text{ kJ/mol} \) (from M&S Ex. 9-3) at \( P_0 = 1 \text{ atm} \) and \( T(P_0) = 273.15 \text{ K} \) so that \( \alpha = -2.71 \times 10^{-10} \text{ Pa}^{-1} = -0.0271 \text{ kbar}^{-1} \). Given the small size of this exponent, for the pressures of interest, the exponential can be expanded and only the first order term kept, which provides the relation:

\[ T_{\text{fus}} / \text{K} = 273.16 - 7.40(P / \text{kbar}) \]

This result is shown for comparison as the dashed line in the figure above. As would be anticipated the result derived via the Clapeyron equation provides the correct behavior (apart from the displacement caused by inaccurate reading of the M&S graph) at low pressures. However, the assumption that \( \Delta_{\text{fus}}V \) and \( \Delta_{\text{fus}}H \) are pressure independent for these large pressures leads to inaccurate predictions at kbar pressures.

**End Aside**

We must now consider how much pressure is likely to be generated by a skater. For skater mass \( m \) and skate area \( A \), the pressure is given by \( P = mg / A \) where \( g \) is the acceleration of gravity (9.806 m s\(^{-2}\)). We can take as a typical body mass \( m = 75 \text{ kg} \). The only difficult thing to estimate is the skate area. The lowest pressure will be obtained by assuming that the entire area of the skate blade contacts the ice. An estimate for the area in this case might be \( A = 20 \text{ cm} \times 3 \text{ mm} = 6 \times 10^{-4} \text{ m}^2 \). But does the entire skate blade really contact the ice at any instant? Probably not. If one assumes that only a fraction (say 1/3) of the length of a curved blade and only the width of an edge of the skate blade contacts the surface, the pressures generated would be much higher. Estimating an edge width to be ~100 \( \mu \text{m} \), the area would now be ~6 \times 10^{-6} \text{ m}^2 \). Using this rather broad spread of estimated skate areas, I computed the melting temperatures tabulated below.

<table>
<thead>
<tr>
<th>Area /m(^3)</th>
<th>Pressure /kbar</th>
<th>( T_f /\text{K} )</th>
<th>( T_f /^\circ\text{C} )</th>
<th>( T_f /^\circ\text{F} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.\times 10^{-4}</td>
<td>0.012</td>
<td>273.07</td>
<td>-0.08</td>
<td>32</td>
</tr>
<tr>
<td>6.\times 10^{-5}</td>
<td>0.12</td>
<td>272.2</td>
<td>-0.9</td>
<td>30</td>
</tr>
<tr>
<td>6.\times 10^{-6}</td>
<td>1.23</td>
<td>261.7</td>
<td>-11.4</td>
<td>11</td>
</tr>
</tbody>
</table>

It would appear that except for the smallest estimates of skate area, the pressure-induced change in temperature is modest. If the lowest area estimate is reasonable, a 75 kg person should be able to skate at temperatures as low as ~11\(^\circ\text{C} \). Of course, the above judgment rests on skating being an equilibrium processes. This analysis has ignored the effects of friction, which are likely to substantially lower the temperature at which skating is possible. (I say this mainly based on the belief that I’ve skated at temperatures lower than -11\(^\circ\text{C} \)).
9. M&S 9-24: Use the vapor pressure data given in Problem 9-7 and the density data given in Problem 9-13 to calculate $\Delta_{vap}H$ for methanol from the triple point (175.6 K) to the critical point (512.6 K). Plot your results.
M&S 9-25: Use the results of the previous problem to plot $\Delta_{vap}S$ of methanol from the triple point to the critical point.
M&S 9-26: Use the vapor pressure data for methanol given in Problem 9-7 to plot $\ln P$ against $1/T$. Using your calculations from problem 9-24, over what temperature range do you think the Clausius-Clapeyron equation will be valid?

(a) & (b) Noting that $\Delta_{vap}H = \rho^{-1}_v - \rho^{-1}_L$, where the $\rho_i$ are molar densities, the Clapeyron equation can be solved for $\Delta_{vap}H$ and written in the form:

$$\Delta_{vap}H = T \left( \frac{dP}{dT} \right)_{vap} \left( \frac{1}{\rho_v} - \frac{1}{\rho_L} \right)$$

$\Delta_{vap}S$ is given by $\Delta_{vap}S = \Delta_{vap}H / T_{vap}$. Given the expressions for $P(T), \rho_v(T)$, and $\rho_L(T)$ provided in M&S problems 9-7 and 9-13 I calculated $\Delta_{vap}H(T)$ and $\Delta_{vap}S(T)$ and $\ln P(T)$ using the Mathcad worksheet shown below. In addition, given the remarkable linearity of the $\ln P$ vs $1/T$, it was of interest to calculate the prediction for $\Delta_{vap}H(T)$ that would be made assuming the validity of the Clausius-Clapeyron equation. Denoting this estimate $\Delta H_{cc}$, the relevant equation is:

$$\Delta H_{cc}(T) = RT^2 \left( \frac{1}{P} \frac{dP}{dT} \right)_{vap}$$

This quantity was also calculated in the Mathcad worksheet shown below. The plots of $\Delta_{vap}H(T)$ and $\Delta_{vap}S(T)$ and $\ln P(1/T)$ follow.

\[
\begin{align*}
p_1 &:= -10.752849 \\
p_2 &:= 16.758207 \\
p_3 &:= -3.603425 \\
p_4 &:= 4.373232 \\
p_5 &:= -2.381377 \\
p_6 &:= 4.572199 \\
dl_1 &:= 2.51709 \\
dl_2 &:= 2.466694 \\
dl_3 &:= -3.066818 \\
dl_4 &:= 1.325077 \\
dv_1 &:= -10.619689 \\
dv_2 &:= -2.556682 \\
dv_3 &:= 3.881454 \\
dv_4 &:= 4.795568 \\
T_c &:= 512.60 K \\
\rho_c &:= 8.40 \text{ mol L}^{-1} \\
T_{tp} &:= 175.6 K \\
x(T) &:= T / T_c \\
P(x) &:= \text{bar} \exp \left[ \frac{p_1}{x} + p_2 + p_3 \cdot x + p_4 \cdot x^2 + p_5 \cdot x^3 + p_6 \cdot (1 - x)^{1.70} \right] \\
\rho_f(x) &:= \rho_c \left[ 1 + dl_1 \cdot (1 - x)^{0.350} + dl_2 \cdot (1 - x) + dl_3 \left( 1 - x^2 \right) + dl_4 \left( 1 - x^3 \right) \right] \\
\rho_v(x) &:= \rho_c \exp \left[ dv_1 \cdot \frac{(1 - x)}{x} + dv_2 \cdot (1 - x)^{0.350} + dv_3 \cdot (1 - x) + dv_4 \cdot (1 - x)^2 \right] \\
\Delta H_{vap}(x) &:= \left( \frac{1}{\rho_v(x)} - \frac{1}{\rho_f(x)} \right) \cdot x \cdot \frac{dP(x)}{dx} \\
\Delta S_{vap}(x) &:= T_c \cdot \left( 1 - \frac{\Delta H_{vap}(x)}{x} \right) \\
\Delta H_{cc}(x) &:= R \cdot T_c \cdot x \cdot \left( \frac{1}{P(x)} \right) \cdot \frac{dP(x)}{dx} 
\end{align*}
\]
The plots of $\Delta_{vap}H(T)$ and $\Delta_{vap}S(T)$ display the behavior expected: both functions approach zero as $T \to T_c$.

More remarkable is the fact that $\ln P$ is very nearly a linear function of $1/T$ over the entire range of temperatures considered: all the way from the triple point to the critical point of the fluid. Over this temperature range the pressure varies by a factor of $10^8$! Such approximately linearity is not confined to methanol, but is observed in many other systems, i.e. in the examples of Ar, ethane, CCl$_4$, and benzene I showed in class. The Clausius-Clapeyron equation predicts $\ln P$ to be linear in $1/T$ when $\Delta_{vap}H$ is temperature independent. But in the present case, and in general, $\Delta_{vap}H$ is far from constant, especially when $T$ approaches $T_c$.

Thus, the Clausius-Clapeyron equation does not provide correct predictions over this whole range of temperatures. To explore the validity of the Clausius-Clapeyron equation further, I calculated $\Delta \overline{H}_{cc}(T)$ as described above and plotted the result (dashed curve) together with the exact values of $\Delta_{vap}\overline{H}(T)$. From this comparison one finds that the estimates of $\Delta_{vap}\overline{H}(T)$ provided by the Clausius-Clapeyron are accurate to about the 5% level for temperatures between $T_{tp}$ and $\sim 0.6T_c$. However, at temperatures higher than $0.8T_c$ the estimates are in error by more than 25%.

It is interesting to conjecture about the origins of the approximate linearity of $\ln P$ versus $1/T$. One can rewrite the Clausius equation in the form:
\[
\frac{1}{P} \left( \frac{dP}{dT} \right)_{vap} = \left\{ \frac{\Delta_{vap} H}{\Delta_{vap} V} \frac{T}{P} \right\} \frac{dT}{T^2} \quad \text{or} \quad \left( \frac{d \ln P}{d(1/T)} \right)_{vap} = -\frac{\Delta_{vap} H}{R \Delta_{vap} Z}
\]

where \( \Delta_{vap} Z = (P \Delta_{vap} V / RT) \). From this last equation, it would seem that the near linearity observed here must stem from the near constancy of the ratio \( (\Delta_{vap} H / \Delta_{vap} Z) \) through the entire temperature range. (Why this ratio should be constant is another question...)

10. This problem examines the quality of corresponding states correlations under sub-critical conditions.

(a) M&S 2-29: Look up the boiling points of the gases listed in Table 2.5 and plot these values versus the critical temperatures \( T_c \). Is there a correlation? Propose a reason to justify your conclusion from the plot.

(b) You should find a good correlation between \( T_b \) and \( T_c \) in part (a), but you should ask yourself whether this is really corresponding states behavior. (What’s being done with the pressure variable?) Use the perspectives provided by Ch. 9 to rationalize why the correlation is as good as it is.

(c) Compare \( T_f \) and \( T_c \) in the same manner as in part (a). Note that \( T_f \) provides a good approximation to the triple-point temperature, \( T_{tp} \) in most cases. Explain why this is true and comment on the quality of the corresponding states behavior you observe.

The data I used for this comparison are tabulated below. I have omitted the He point, since it is not expected to follow corresponding states correlations (due to its quantal nature), and I have also added a few more substances to the list in Table 2.5 of M&S.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( T_c )/K</th>
<th>( P_c )/bar</th>
<th>( T_f )/K</th>
<th>( T_b )/K</th>
<th>( \Delta T )/K</th>
<th>T-CS/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>44.4</td>
<td>26.6</td>
<td>24.6</td>
<td>27.1</td>
<td>-1.5</td>
<td>25.6</td>
</tr>
<tr>
<td>Argon</td>
<td>151.0</td>
<td>49.3</td>
<td>83.9</td>
<td>87.3</td>
<td>1.7</td>
<td>89.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>32.9</td>
<td>12.8</td>
<td>14.0</td>
<td>20.4</td>
<td>-3.7</td>
<td>16.7</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>126.2</td>
<td>34.0</td>
<td>63.3</td>
<td>77.4</td>
<td>-1.7</td>
<td>75.7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>154.6</td>
<td>50.4</td>
<td>54.3</td>
<td>90.2</td>
<td>2.0</td>
<td>92.1</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>132.9</td>
<td>34.9</td>
<td>68.1</td>
<td>81.7</td>
<td>-1.5</td>
<td>80.1</td>
</tr>
<tr>
<td>Chlorine</td>
<td>416.9</td>
<td>79.9</td>
<td>172.0</td>
<td>235.1</td>
<td>15.7</td>
<td>250.9</td>
</tr>
<tr>
<td>Water</td>
<td>647.1</td>
<td>220.6</td>
<td>273.2</td>
<td>373.2</td>
<td>54.5</td>
<td>427.7</td>
</tr>
<tr>
<td>Ammonia</td>
<td>405.3</td>
<td>111.3</td>
<td>195.4</td>
<td>239.7</td>
<td>22.0</td>
<td>261.8</td>
</tr>
<tr>
<td>Methane</td>
<td>190.5</td>
<td>46.0</td>
<td>90.6</td>
<td>111.5</td>
<td>1.3</td>
<td>112.8</td>
</tr>
<tr>
<td>Ethane</td>
<td>305.3</td>
<td>48.7</td>
<td>89.8</td>
<td>184.6</td>
<td>3.1</td>
<td>187.7</td>
</tr>
<tr>
<td>Propane</td>
<td>369.9</td>
<td>42.5</td>
<td>85.5</td>
<td>231.1</td>
<td>0.7</td>
<td>231.8</td>
</tr>
<tr>
<td>Butane</td>
<td>425.2</td>
<td>38.0</td>
<td>134.8</td>
<td>272.7</td>
<td>-2.6</td>
<td>270.1</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>407.9</td>
<td>36.4</td>
<td>113.6</td>
<td>261.4</td>
<td>-3.8</td>
<td>257.6</td>
</tr>
<tr>
<td>Pentane</td>
<td>469.7</td>
<td>33.6</td>
<td>143.4</td>
<td>309.2</td>
<td>-6.2</td>
<td>303.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>561.8</td>
<td>48.8</td>
<td>278.7</td>
<td>353.3</td>
<td>16.8</td>
<td>370.1</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>556.4</td>
<td>45.6</td>
<td>250.0</td>
<td>349.9</td>
<td>3.2</td>
<td>353.1</td>
</tr>
<tr>
<td>224-Trimethylpantane</td>
<td>544.0</td>
<td>25.7</td>
<td>165.8</td>
<td>372.4</td>
<td>-15.1</td>
<td>357.3</td>
</tr>
<tr>
<td>Bromine</td>
<td>588.0</td>
<td>103.0</td>
<td>266.0</td>
<td>331.9</td>
<td>30.9</td>
<td>362.8</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>461.0</td>
<td>64.8</td>
<td>189.8</td>
<td>292.6</td>
<td>49.5</td>
<td>342.2</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>324.7</td>
<td>83.1</td>
<td>159.0</td>
<td>188.1</td>
<td>13.6</td>
<td>201.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>513.9</td>
<td>61.4</td>
<td>158.5</td>
<td>351.6</td>
<td>10.7</td>
<td>362.3</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>466.7</td>
<td>36.4</td>
<td>156.9</td>
<td>307.8</td>
<td>-3.8</td>
<td>304.0</td>
</tr>
</tbody>
</table>

Plots of the correlations between \( T_b \), \( T_f \), and \( T_c \) are provided below (left-hand panel).
One finds that the correlation between $T_b$ and $T_c$ is fairly good, but far from perfect. A listing of some characteristics of this and other correlations is provided below.

<table>
<thead>
<tr>
<th></th>
<th>$T_f$</th>
<th>$T_b$</th>
<th>$T$-CS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fit</td>
<td>R2</td>
<td>0.819</td>
<td>0.980</td>
</tr>
<tr>
<td>Fit</td>
<td>slope</td>
<td>0.388</td>
<td>0.622</td>
</tr>
<tr>
<td>Fit</td>
<td>std. err.</td>
<td>33</td>
<td>17</td>
</tr>
<tr>
<td>Ratio</td>
<td>average</td>
<td>0.41</td>
<td>0.611</td>
</tr>
<tr>
<td>Ratio</td>
<td>std. dev.</td>
<td>0.1</td>
<td>0.032</td>
</tr>
</tbody>
</table>

The 1st three rows labeled “Fit” refer to linear fits (with a constraint of zero intercept) of $T_b$ and $T_f$ versus $T_c$. The final two rows refer to ratios $T_b / T_c$ and $T_f / T_c$ — i.e. to the reduced boiling and melting points. From these data one finds that the boiling point of a substance is located at $(0.61\pm0.03)T_c$.

Is this behavior an example of the law of corresponding states? Yes, but the law of corresponding states has not been rigorously applied here. The boiling point refers to a pressure of 1 atm, and this pressure represents different reduced conditions (i.e. $P_r=P/P_c$) for the different substances. A correct corresponding states analysis entails comparison of substances under the same ($T_r, P_r$) conditions, not the same ($T_r, P$) conditions. What should be done here is to compare the temperatures (or reduced temperatures) for which the coexisting liquid-vapor pressure reaches a particular reduced value. For the range of substances considered here, 1 atm corresponds to reduced pressures $0.01 \leq P_r \leq 0.04$, with an average value of $P_r = 0.024$. It is possible to use the Clausius-Clapeyron equation and the enthalpies of vaporization of these liquids to estimate true corresponding states temperatures by computing the temperature at which $P = 0.024P_c$ for all of the substances. The last two
columns labeled \(\Delta T\) and \(T-CS\) show the temperature change and corrected temperature for a true corresponding states comparison. The right-hand figure below shows the effect of making this more proper corresponding states comparison.

The proper and improper comparisons do not differ appreciably. From the tabulated values of \(\Delta T\), one finds that, for most simple substances, the differences in the normal boiling temperatures and the more proper corresponding states temperatures is small. Large corrections are found primarily for substances with strong hydrogen bonding interactions. Since these latter substances are not expected to fit into the same corresponding states correlations as simple non-hydrogen bonding substances, the quality of the more proper corresponding states analysis is little changed (see the statistics table).

The normal melting point and triple point of most substances should not differ by more than a degree. Examples culled from the textbook are [substance \((T_{tp}/T_f)\): O\(_2\) (54.3 / 54.75 K), I\(_2\) (386 / 387 K), benzene (278.7 / 278.7 K), methane (90.68 / 90.7 K), and water (273.16 / 273.15). Why should these temperatures be so similar? The difference between the triple point and the normal melting point of a substance can be estimated from

\[
\frac{\Delta T}{T} = \frac{T_f - T_{tp}}{T_{tp}} \approx \left(\frac{\Delta_{fus} V}{\Delta_{fus} H}\right)_{tp} \Delta P
\]

where \(\Delta P = (1 \text{ atm} - P_{tp})\). Consider benzene as a typical case (since data is available from M&S p. 362). \(\Delta_{fus} V = 10.3 \text{ cm}^3 \text{ mol}^{-1}\) and \(\Delta_{fus} H = 9.95 \text{ kJ mol}^{-1}\) so \(\Delta T/T = 1.03 \times 10^{-4}\) \(\Delta P/\text{bar} \approx 10^{-4}\) (since \(P_{tp} < 1\) bar). This result is typical in the sense that the vapor pressures of solids are usually less than 1 bar, and the ratio of \((\Delta_{fus} V / \Delta_{fus} H)\) is not expected to be greatly different from the value \(10^{-4}\). Thus, in general one should expect \(T_{tp} = T_f\) to within 1% or better.

The triple point is a unique point in the phase diagram of any pure substance. Having confirmed that the normal melting point provides a good measure of the temperature at the triple point, if corresponding states correlations were to apply to both the fluid and solid states, one would expect there to be a good correlation between \(T_f\) and \(T_c\). The comparisons made here show that there is some degree of correlation, but it is much poorer than is the case with \(T_v\). The fusion or triple point temperature of a substance can be estimated to be \((0.4 \pm 1)T_v\), but the scatter about this correlation is considerable. The reason for the scatter is that the details of molecular shape and interaction type are more important for determining the properties of ordered solid phases than they are for determining the properties of disordered fluid phases. Thus, the underlying idea upon which corresponding states behavior rests, that molecular details are unimportant apart from a generic size and interaction strength parameter, is a poorer approximation for solid phases.