1. At \(-5.0 \, ^\circ\text{C}\), the vapor pressure of ice is 3.013 mm and that of liquid water is 3.163 mm. Calculate \(\Delta G\) for the change of one mole of liquid water at \(-5.0 \, ^\circ\text{C}\) to solid at \(-5.0 \, ^\circ\text{C}\).

**ANS:**
The system will not be in equilibrium, so \(\Delta G\) is not zero. We have to find a series of steps between the initial and final states. For \(\Delta S\), we raised the temperature to 0 ° but won’t do that now because of the difficulty of calculating \(\Delta G\) for a change in T. The clue to the solution is given by the inclusion of vapor pressures in the problem. We can calculate \(\Delta G\) for a change in pressure at constant temperature. The alternative path for the process has three steps, all at \(-5 \, ^\circ\text{C}\):

- **Step 1:** Liquid water at 3.163 mm \(\rightarrow\) vapor at 3.163 mm.
- **Step 2:** Vapor at 3.163 mm \(\rightarrow\) vapor at 3.013 mm.
- **Step 3:** Vapor at 3.013 mm \(\rightarrow\) solid water at 3.013 mm.

Steps (1) and (3) are equilibrium processes (\(\Delta G = 0\)), so the total \(\Delta G\) is the \(\Delta G\) of step (2).

\[
\Delta G = nRT \ln \frac{P_2}{P_1} = 1(8.314)(268.2) \ln \frac{3.013}{3.163} = -108.3 \text{ J}
\]

2. Calculate the pressure at which the conversion of graphite to diamond would become thermodynamically possible.

(a) At 298.15 K.

(b) At 1000 K.

The densities of diamond and graphite are 3.513 g mL\(^{-1}\) and 2.260 g mL\(^{-1}\) respectively, \(\Delta_r \overline{H}^\circ = +1.895 \text{ kJ mol}^{-1}\) and \(\Delta_r \overline{S}^\circ = -3.255 \text{ J mol}^{-1} \text{K}^{-1}\). All of these values may be considered to be independent of temperature

\[\text{C (graphite)} \rightarrow \text{C (diamond)}\]

**ANS:**

(a) At constant temperature

\[
dG = VdP
\]
or

\[
d(\Delta_r \overline{G}) = (\Delta_r \overline{V})dP
\]
equation (i)

where \(\Delta_r G_{298.15 \, \text{K}}^\circ\)

\[
= \Delta \overline{H}^\circ - T \Delta \overline{S}^\circ
\]
\[
= 1895 \text{ J/mol} - (298.15 \, \text{K})(-3.255 \, \text{J/mol})
\]
\[
= 2865.48 \, \text{J mol}^{-1}
\]
and \( \Delta_rV = \bar{V}(\text{diamond}) - \bar{V}(\text{graphite}) \)
\[
= \frac{12.011 \text{ g mol}^{-1}}{3.513 \text{ g mL}^{-1}} - \frac{12.011 \text{ g mol}^{-1}}{2.260 \text{ g mL}^{-1}}
\]
\[
= -1.895_{59} \text{ mL mol}^{-1}
\]
\[
= -1.895_{59} \times 10^{-3} \text{ L mol}^{-1}
\]

So, from equation (i), integrating with \( \Delta_rV \) taken as constant (since densities are constant)
\[
\int_1^2 d(\Delta_rG) = \int_1^2 (\Delta_rV) dP = (\Delta_rV) \int_1^2 dP
\]
\[
\therefore \Delta_rG_2 - \Delta_rG_1 = \Delta_rV(P_2 - P_1)
\] equation (ii)

Set \( P_1 = 1 \text{ bar}, \) Then \( \Delta_rG_1 = \Delta_rG^\ominus = 2865.48 \text{ J mol}^{-1} \)
\( P_2 \) will be the pressure required for \( \Delta_rG_2 = 0 \) (thermodynamic possibility)
\[
\therefore 0 - 2854.48 \text{ J mol}^{-1} = -1.895_{59} \times 10^{-3} \text{ L mol}^{-1} (P_2 - 100 \text{ kPa})
\]
\[
\therefore P_2 = 1.512 \times 10^6 \text{ kPa} \quad \text{or} \quad 1.512 \times 10^4 \text{ bar}
\]

(b) at 1000 K,
\[
\Delta_rG_{1000 K}^\ominus = \Delta_rH^\ominus - T\Delta_rS^\ominus
\]
\[
= 1895 \text{ J mol}^{-1} - (1000 \text{ K})(-3.255 \text{ J mol}^{-1} \cdot \text{K})
\]
\[
= 5150 \text{ J mol}^{-1}
\]

Again using equation (ii),
\[
0 - 5150 \text{ J mol}^{-1} = -1.895_{59} \times 10^{-3} \text{ L mol}^{-1} (P_2 - 100 \text{ kPa})
\]
\[
\therefore P_2 = 2.717 \times 10^6 \text{ kPa} \quad \text{or} \quad 2.717 \times 10^4 \text{ bar}
\]
\[
\therefore \text{ A higher pressure is required at higher temperature. So, why do you think high temperatures are used to make artificial diamonds?}
\]

3. Calculate the freezing point of benzene at a pressure of 2000 atm. The normal freezing point is 5.533 °C and the densities of liquid and solid benzene are 0.8780 g cm\(^{-3}\) and 0.900 g cm\(^{-3}\), respectively. \( \Delta H_{\text{FUS}} = 10.58 \text{ kJ mol}^{-1} \).

ANS:

Using the Clapeyron equation.
\[
\frac{dP}{dT} = \frac{\Delta H_{\text{FUS}}}{TM \Delta V_{\text{FUS}}} \quad \text{or} \quad \frac{\Delta P}{\Delta T} = \frac{\Delta H_{\text{FUS}}}{TM \Delta V_{\text{FUS}}}.
\]

where \( \Delta V_{\text{FUS}} = \bar{V}(l) - \bar{V}(s) = 78.11 \text{ g mol}^{-1} \cdot \text{cm}^3 - 78.11 \text{ g mol}^{-1} \cdot \text{cm}^3 \)
\[
\Delta V_{\text{FUS}} = 2.11 \text{ cm}^3 \text{ mol}^{-1} = 2.11 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}
\]
\[
\therefore \frac{\Delta P}{\Delta T} = \frac{10.58 \times 10^3 \text{ J K}^{-1} \text{ mol}^{-1}}{2.11 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \times 278.68 \text{ K}} = 1.799 \times 10^7 \text{ Pa K}^{-1}
\]

Now \( \Delta P = 2000 - 1 \text{ atm} = 2.025 \times 10^8 \text{ Pa} \)
\[
\therefore \Delta T = \frac{2.025 \times 10^8 \text{ Pa}}{1.799 \times 10^7 \text{ Pa K}^{-1}} = 11.26 \text{ K}
\]
\[
\therefore T_M (2000 \text{ atm}) = (278.68 + 11.26) \text{ K} = 289.94 \text{ K}
\]
4. Using the data provided for benzene, calculate the vapor pressure of solid benzene at –20 ºC.

Benzene:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>80.10 ºC</td>
</tr>
<tr>
<td>Melting point</td>
<td>5.53 ºC</td>
</tr>
<tr>
<td>( \Delta H_{\text{VAP}} )</td>
<td>30.76 kJ mol(^{-1})</td>
</tr>
<tr>
<td>( \Delta H_{\text{FUS}} )</td>
<td>10.59 kJ mol(^{-1})</td>
</tr>
</tbody>
</table>

ANS:
We assume that the triple point occurs at the same temperature as the normal melting point. Then we can apply the Clausius-Clapeyron equation to the vaporization curve to find the vapor pressure of liquid benzene at the triple point (taken as 5.53 ºC). Remember that the vapor pressure at the normal boiling point is 1 atm.

Then

\[
\ln \left( \frac{P}{1 \text{ atm}} \right) = \frac{\Delta H_{\text{VAP}}}{8.314 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{278.68 \text{ K}} - \frac{1}{353.25 \text{ K}} \right)
\]

Hence \( P_t = 6.07 \times 10^{-2} \) atm. (vapour pressure at triple point)

But at the triple point, solid is in equilibrium with the vapour at this same vapour pressure. We can now apply the Clausius-Clapeyron equation to the sublimation curve to determine the vapour pressure (p) at –20 ºC. For the sublimation curve we need

\[
\Delta H_{\text{SUB}} = \Delta H_{\text{FUS}} + \Delta H_{\text{VAP}} = 41.35 \times 10^3 \text{ J mol}^{-1}
\]

Then

\[
\ln \left( \frac{p}{6.07 \times 10^{-2}} \right) = \frac{-41350 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{253.15 \text{ K}} - \frac{1}{278.68 \text{ K}} \right)
\]

Hence \( p = 1.00 \times 10^{-2} \) atm
(Vapour pressure of solid benzene at –20 ºC)
5. The normal melting point of naphthalene (molar mass = 128.2 g mol\(^{-1}\)) is 80.2 °C and it rises by 2.32 °C when the pressure increases by 100 atmospheres. It boils at 217.9 °C and it's molar enthalpy of vaporization is 40.5 kJ mol\(^{-1}\). The density of solid naphthalene is 1.15 g mL\(^{-1}\) and that of the liquid is 10% less. Calculate.

(a) The molar enthalpy of fusion of naphthalene.

ANS:

\[
\bar{V}(s) = \frac{128.2 \text{ g mol}^{-1}}{1.15 \text{ g mL}^{-1}}
\]

\[
\therefore \bar{V}(s) = 111.5 \text{ mL} \cdot \text{mol}^{-1}
\]

\[
\bar{V}(l) = \frac{128.2 \text{ g mol}^{-1}}{1.035 \text{ g mL}^{-1}}
\]

\[
\therefore \bar{V}(l) = 123.9 \text{ mL} \cdot \text{mol}^{-1}
\]

\[
\Delta \bar{V}_{\text{FUS}} = 123.9 - 111.5
\]

\[
\therefore \Delta \bar{V}_{\text{FUS}} = 12.4 \text{ mL} \cdot \text{mol}
\]

\[
\Delta H_{\text{FUS}} = \frac{2.32 \text{ K}}{100 \times 101.3 \text{ kPa}} = \frac{(353.35 \text{ K})(0.0124 \text{ L/mol})}{\Delta H_{\text{FUS}}}
\]

\[
\therefore \Delta H_{\text{FUS}} = 19.13 \text{ kJ} \cdot \text{mol}^{-1}
\]

(b) The vapor pressure of liquid naphthalene at the triple point (you may assume that this is the same temperature as the normal melting point).

ANS:

Apply the Clausius-Clapeyron equation to the vaporization curve, assuming that the triple point temperature is the same as the melting point,

\[
\ln\left(\frac{P}{P_{\text{atm}}}\right) = -\frac{-\Delta H_{\text{VAP}}}{R} \left(\frac{1}{T_{\text{mpt}}} - \frac{1}{T_{\text{bpt}}}\right)
\]

\[
\therefore \ln(P) = -\frac{-40500 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} \left(\frac{1}{353.35 \text{ K}} - \frac{1}{491.05 \text{ K}}\right)
\]

\[
\therefore \ln(P) = -3.8659
\]

\[
\therefore P = 2.09 \times 10^{-2} \text{ atm} = 2.12 \text{ kPa} \text{ (vapour pressure at the triple point)}
\]

(c) The vapor pressure of solid naphthalene at 75.0 °C.

ANS:

\[
\Delta H_{\text{SUB}} = \Delta H_{\text{FUS}} + \Delta H_{\text{VAP}}
\]

\[
\therefore \Delta H_{\text{SUB}} = 19.13 \text{ kJ} \cdot \text{mol}^{-1} + 40.5 \text{ kJ} \cdot \text{mol}^{-1}
\]
The vapor pressure of solid naphthalene and liquid naphthalene are the same at the triple point. Apply the Clausius-Clapeyron equation to the sublimation curve:

\[ \ln \left( \frac{P}{2.12 \text{ kPa}} \right) = \frac{-59630 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} (0.0028723 - 0.0028301) \]

\[ \ln \left( \frac{P}{2.12 \text{ kPa}} \right) = -0.303 \ln \left( \frac{P}{2.12 \text{ kPa}} \right) \]

\[ \ln \left( \frac{P}{2.12 \text{ kPa}} \right) = 0.738 \]

\[ P = 1.56 \text{ kPa} \] (vapor pressure of solid at 75 °C)

(d) The free energy change when 1.00 mol of supercooled liquid naphthalene solidifies at 75.0 °C.

\[ \Delta G = ? \]

\[ \Delta G = 0 \]

\[ \Delta G_1 = 0 \]

\[ \Delta G_2 = nRT \ln \left( \frac{P_1}{P_2} \right) \]

\[ = 1 \times 8.314 \times 348.15 \times \ln \left( \frac{1.73}{1.56} \right) \]

\[ \Delta G = -293 \text{ J} \cdot \text{mol}^{-1} \] (spontaneous of course)
NOTE: That (l) naphthalene is in equilibrium with vapour at 1.73 kPa at 75 °C (see above), so \( \Delta G_1 = 0 \). Likewise, solid naphthalene is equilibrium with vapour at 1.56 kPa at 75 °C (part (c) above) and \( \therefore \Delta G_3 = 0 \). This part of the problem is the same as problem #1 in this problem set.

6. 0.810 g of hydrocarbon of the type; H(CH\(_2\))\(_n\)H, is dissolved in 190 g of ethylene bromide. The freezing point of the solution is 0.53 K lower than the pure solvent \( (K_F = 12.4 \text{ K mol}^{-1}) \). Calculate the value of \( n \) in the formula of the hydrocarbon. What assumption is it necessary to make about the hydrocarbon?

ANS:
Assume that the hydrocarbon is **non-volatile**.

Then \[ \Delta T_F = K_F m \]

\[ m = \frac{\Delta T_F}{K_F} = \frac{0.53 \text{ K}}{12.4 \text{ K mol}^{-1}} = 0.04274 \text{ molal} \]

\[ \therefore 1000 \text{ g ethylene bromide contains } 0.04274 \text{ mol hydrocarbon} \]

\[ 190 \text{ g ethylene bromide contains } \frac{190 \times 0.04274}{1000} \text{ mol hydrocarbon} \]

\[ = 0.008121 \text{ mol hydrocarbon} \]

But, from question, this hydrocarbon has a mass of 0.810 g

\[ \therefore \text{ Molar mass of the hydrocarbon} = \frac{0.810 \text{ g}}{0.008121 \text{ mol}} \]

\[ = 100 \text{ g mol}^{-1} \]

For H(CH\(_2\))\(_n\)H, the molar mass \( = 14n + 2 \)

\[ 14n + 2 = 100 \]

\[ \therefore 14n = 98 \]

\[ \therefore n = \frac{98}{14} = 7 \]

\[ \therefore \text{ The formula is H(CH}_2\text{)}_7\text{H}. \]

7. Bovine serum albumin (BSA) has a molar mass of 65000 g mol\(^{-1}\). Calculate the osmotic pressure of a solution of 2.0 g BSA in 0.100 L of water at 25.0 °C.

ANS:
Assume \( V_{\text{SOLN}} = 0.100 \text{ L} \)

\[ C_2 = \frac{M_2}{V} = \frac{2 \text{ g}}{65000 \text{ g mol}^{-1}} = 3.077 \times 10^{-4} \text{ mol L}^{-1} \]

\[ \pi = C_2RT \text{ where } C_2 \text{ in mol L}^{-1}, R \text{ in L atm, } \pi \text{ in atm} \]

\[ \therefore \pi = 3.077 \times 10^{-4} \text{ mol L}^{-1} \times 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \]

\[ = 7.5 \times 10^{-3} \text{ atm} \]

8. The normal boiling point of nitrobenzene is 210.9 °C. If the vapor pressure at 180 °C is 353.2 mm Hg, what is the vapor pressure at 200 °C?
ANS:
This problem has two steps. Since \( \Delta H \), isn't given, you must calculate it. Remember that the normal boiling point is at 1 atm. You have two pressures with corresponding temperatures, and, using the Clausius-Clapeyron equation

\[
\Delta H_v = 8.314 \left( \ln \frac{760}{353.2} \right) \left[ \frac{484.1(453.2)}{484.1 - 453.2} \right] = 45.23 \text{ kJ mol}^{-1}
\]

In order to obtain the vapor pressure at a given temperature, use the Clausius-Clapeyron equation again and solve for the desired quantity.

\[
\ln P_2 = \ln P_1 + \left( \frac{\Delta H_v}{R} \right) \left( \frac{T_2 - T_1}{T_1} \right)
\]

Choosing 353.2 mm as \( P_1 \),

\[
\ln P_2 = \ln(353.2) + \left( \frac{45.23 \times 10^3}{8.314} \right) \left[ \frac{473.2 - 453.2}{473.2(453.2)} \right] = 5.8670 + 0.5074
\]

\[ P_2 = 586.6 \text{ mm Hg} \]

9. When 4.07 g of a new water soluble polymer was dissolved in 82.4 mL of water the measured osmotic pressure was 6.23 kPa at 22.0 \(^\circ\)C.
(a) Calculate the molar mass of the polymer.
ANS:
\[ \pi = C_2RT \text{ so } C_2 = \frac{6.23 \text{ Pa}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 295.15 \text{ K}} = 2.53 \times 10^{-3} \text{ mol L}^{-1} \]

\[ \therefore \text{ molar mass} = \frac{4.07 \text{ g}}{2.53 \times 10^{-3} \text{ mol L}^{-1} \times 82.4 \times 10^{-3} \text{ L}} = 1.95 \times 10^4 \text{ g mol}^{-1} \]

(b) Calculate the freezing point of the solution.
ANS:
Assuming the density of the water is 1.0 g ml\(^{-1}\), the molality is
\[ m = \frac{4.07 \text{ g}}{82.4 \times 10^{-3} \text{ kg}} = 0.0253 \text{ m} \]

\[ \Delta T = K_f m \]
\[ \therefore \Delta T = 1.86 \text{ K m}^{-1} \times 0.0253 \text{ m} = 0.047 \text{ K} \]

So the freezing point of the solution is still 22.0 \(^\circ\)C to 3 significant digits - the change in fp is barely measurable.

10. Phenol (C\(_6\)H\(_5\)OH) is partially dimerized in the solvent bromoform. When 2.58 g of phenol is dissolved in 100 g of bromoform, the bromoform freezing point is lowered by 2.37 \(^\circ\)C. Pure bromoform has a molal freezing-point-depression
constant of 14.1 °C kg mol⁻¹ and freezes at 8.3 °C. Calculate the equilibrium constant, $K_m$, for the dimerization reaction of phenol in bromoform at 6 °C, assuming an ideally dilute solution.

\[
2 \text{C}_6\text{H}_5\text{OH} \rightleftharpoons (\text{C}_6\text{H}_5\text{OH})_2
\]

**ANS:**

\[
\Delta T = K_f m_a
\]

\[
2.37 = 14.1 m_a
\]

∴ $m_a = 0.1681 \text{ mol kg}^{-1}$  \hspace{1cm} (i)

where $m_a$ is the apparent molality of the phenol. *(i.e. based on actual # mole present at equilibrium)*

Also $m_p = \left( \frac{2.58 \text{ g}}{94.11 \text{ g mol}^{-1}} \right) / 0.100 \text{ kg}

∴ $m_p = 0.2741 \text{ mol kg}^{-1}$  \hspace{1cm} (ii)

where $m_p$ is the molality of the phenol if it it were all present as monomer *(i.e. no dimerization).*

So, in molalities,

<table>
<thead>
<tr>
<th></th>
<th>2 C₆H₅OH</th>
<th>(C₆H₅OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (all monomer)</td>
<td>0.2741</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>−2x</td>
<td>+x</td>
</tr>
<tr>
<td>E</td>
<td>(0.2741 − 2x)</td>
<td>x</td>
</tr>
</tbody>
</table>

∴ At equilibrium, actual # mole of solute per kilogram of solvent = $(0.2741 − 2x) + x = 0.2741 − x$

But from (i) above, this # of mole also $= 0.1681$

∴ $0.2741 − x = 0.1681$

∴ $x = 0.1060 \text{ mol}$

Finally,

\[
K_m = \frac{(m_p)_{eq}^2}{(m_p)_{eq}^2} = \frac{x}{(0.2741 − 2x)^2}
\]

\[
= \frac{0.1060}{(0.2741 − 2(0.1060))^2}
\]

\[
= 27.5
\]