1. 40 points.

(a) Plot the vapor pressure of water over a solution of mannitol as a function of the mole fraction of mannitol. The vapor pressure of pure water at 298 K is 23.8 torr. **Solution:** According to Raoult’s law, the vapor pressure of the solvent is proportional to its mole fraction, so the curve is a straight line starting at $P_{\text{water}}^*$ for $X = 1$ and decreasing towards 0 at $X = 0$.

(b) Sketch a reaction diagram for the reaction

$$\text{CH}_3(g) + \text{HCl}(g) \rightarrow \text{CH}_4(g) + \text{Cl}(g)$$

which has an activation energy of 6 kJ mol$^{-1}$ and a $\Delta_{\text{rxn}}E$ of $-8$ kJ mol$^{-1}$.

(c) Find the $\Delta_{\text{rxn}}G^\circ$ and $K_{eq}$ at 298 K for the reaction

$$\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g).$$

**Solution:** This is the formation reaction for 2.00 mol of NH$_3$, so we use twice the free energy of formation: $\Delta_{\text{rxn}}G^\circ = 2\Delta fG^\circ = -32.90 \text{kJ}$. The equilibrium constant is therefore

$$K_{eq} = e^{-\Delta_{\text{rxn}}G^\circ/(RT)} = e^{32900/[(8.3145)(298)]} = e^{13.3} = 5.97 \cdot 10^5.$$

(d) Write the expression for $K_p$ for the above reaction. **Solution:**

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2}^2P_{\text{H}_2}^3}$$

2. Start with an osmotic cell where the volume of the cell is 10. ml and the volume of the bath is 100. ml. We first add 0.100 mmol B to the cell. Neither B nor C can penetrate the semipermeable membrane. What is the minimum number of moles C that must be added to the bath to get a pressure difference of 0.10 bar at 298 K? **Solution:** We can show that the pressure difference, as you might expect, is proportional to the difference
in concentrations:

\[
\mu_{A}^{\text{bath}} = \mu_{A}^{\star}(P^\circ) + V_{m}(P + \Pi_{\text{bath}} - P^\circ) + RT \ln \alpha_{A}^{\text{bath}}
\]

\[
\ln \alpha_{A}^{\text{bath}} = \ln X_{A}^{\text{bath}} = \ln(1 - X_{C}) \approx -X_{C}
\]

\[
\mu_{A}^{\text{bath}} \approx \mu_{A}^{\star}(P^\circ) + V_{m}(P + \Pi_{\text{bath}} - P^\circ) - RT X_{C}
\]

\[
\mu_{A}^{\text{cell}} \approx \mu_{A}^{\star}(P^\circ) + V_{m}(P + \Pi_{\text{cell}} - P^\circ) - RT X_{B}
\]

\[
V_{m}\Pi_{\text{bath}} - RT X_{C} = V_{m}\Pi_{\text{cell}} - RT X_{B}
\]

\[
(\Delta \Pi = \Pi_{\text{cell}} - \Pi_{\text{bath}} &= \frac{RT}{V_{m}}(X_{B} - X_{C}) = RT([B] - [C])
\]

Then we solve for [C] and use that to find the number of moles C that have to be added to the bath:

\[
[C] = [B] - \frac{\Delta \Pi}{RT} = \frac{n_{B}}{V_{B}} - \frac{\Delta \Pi}{RT}
\]

\[
n_{C} = V_{C}[C] = V_{C} \left[ \frac{n_{B}}{V_{B}} - \frac{\Delta \Pi}{RT} \right]
\]

\[
= (0.100 \text{ L}) \left[ \frac{1.00 \cdot 10^{-4} \text{ mol}}{0.010 \text{ L}} - \frac{0.10 \text{ bar}}{(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})(298 \text{ K})} \right]
\]

\[
= 5.96 \cdot 10^{-4} \text{ mol} = 0.60 \text{ mmol.}
\]

3. Write “+” or “−” or “0” to indicate whether \(\Delta_{\text{rxn}}S^\circ\) of each of the following processes is likely to be positive, negative, or zero.

<table>
<thead>
<tr>
<th>Process</th>
<th>(\Delta_{\text{rxn}}S^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2NO(g) + O_{2}(g) \rightarrow 2NO_{2}(g)</td>
<td>[ ]</td>
</tr>
<tr>
<td>formation reaction of NaCl(s)</td>
<td>[ ]</td>
</tr>
<tr>
<td>Na(s) + \frac{1}{2}Cl_{2}(g) \rightarrow NaCl(s)</td>
<td>[ ]</td>
</tr>
<tr>
<td>formation reaction of Cl_{2}(g)</td>
<td>0</td>
</tr>
<tr>
<td>Cl_{2}(g) \rightarrow Cl_{2}(g)</td>
<td>[ ]</td>
</tr>
<tr>
<td>combustion of CH_{4}(g)</td>
<td>[ ]</td>
</tr>
<tr>
<td>CH_{4} + 3O_{2}(g) \rightarrow CO_{2}(g) + 2H_{2}O(l)</td>
<td>[ ]</td>
</tr>
<tr>
<td>sublimation of CO_{2}(s)</td>
<td>+</td>
</tr>
<tr>
<td>CO_{2}(s) \rightarrow CO_{2}(g)</td>
<td>[ ]</td>
</tr>
</tbody>
</table>

4. Calculate the overall change in volume of the gases for the reaction

\[
N_{2}O_{4}(g) \rightarrow N_{2}(g) + 2O_{2}(g)
\]

carried out adiabatically at 1.00 bar, starting from 0.100 mol \(N_{2}O_{4}\) at 298 K.
Solution: We can calculate the final temperature using the expression for the adiabatic flame temperature. The $\Delta_{\text{rxn}} H^\circ$ is equal to $-1$ times the enthalpy of formation for $\text{N}_2\text{O}_4$:

$$T_2 = 298 \, \text{K} - \frac{\Delta_{\text{rxn}} H}{C_P(\text{products})} = 298 \, \text{K} - \frac{-(9.16 \, \text{kJ mol}^{-1})(10^3 \, \text{J/kJ})}{(29.088 + 2 \cdot 29.355) \, \text{J K}^{-1} \, \text{mol}^{-1}} = 402 \, \text{K}$$

Then we can use the ideal gas law to calculate the volume of the 0.3 moles of product at the final temperature and the volume of the 0.1 mole of reactant at the initial temperature. We want the difference:

$$\Delta_{\text{rxn}} V^\circ = V_{\text{prod}} - V_{\text{react}} = \frac{n_{\text{prod}} RT_2}{P^\circ} - \frac{n_{\text{react}} RT_1}{P^\circ}$$

$$= \frac{R}{P^\circ} [n_{\text{prod}} T_2 - n_{\text{react}} T_1]$$

$$= \frac{0.083145 \, \text{bar L K}^{-1} \, \text{mol}^{-1}}{1.00 \, \text{bar}} [(0.300 \, \text{mol})(402 \, \text{K}) - (0.100 \, \text{mol})(298 \, \text{K})] = 7.55 \, \text{L}.$$

\[3\]