1. One mole of an ideal gas at 27 °C and 1 atm. is heated. It expands at constant pressure to T = 327 °C. You are given that C_p = 20.8 J/K•mol.

a) Calculate the work done on the gas during this process.

\[ \Delta V = \frac{nRT_f}{P} - \frac{nRT_i}{P} = \frac{nRT_f - nRT_i}{P} \]

\[ W = -P \Delta V = -(1\text{ atm})(24.6\text{ L}) = -24.6\text{ L} \cdot \text{atm} = -24.6\text{ L} \cdot \text{atm} \left( \frac{4.1845 \text{ J}}{0.04129 \text{ J/mol K}} \right) \]

\[ = -24.6\text{ L} \cdot \text{atm} \cdot \left( \frac{4.1845 \text{ J}}{0.04129 \text{ J/mol K}} \right) = -24.6\text{ L} \cdot \text{atm} \cdot 100 \text{ kJ/mol K} = -2.49 \text{ kJ} \]

b) Calculate \( \Delta H \) for this process.

Assuming \( C_p \) is constant from 27°C to 327°C:

\[ \Delta H = C_p \Delta T = (20.8 \text{ J/K mol})(200\text{ K}) = 6.24 \text{ kJ/mol} \]

i.e. 6.24 kJ/mol, \( \Delta H = 6.24 \text{ kJ} \)

c) Calculate the heat absorbed by the gas.

For a reversible expansion such as this,

\[ q = \Delta H = 6.24 \text{ kJ} \]

d) Calculate \( \Delta E \) for this process.

\[ \Delta E = \Delta H + W = 6.24 \text{ kJ} + (-2.49 \text{ kJ}) = 3.75 \text{ kJ} \]
2. The shells of marine organisms contain CaCO₃ largely in the crystalline form known as calcite. There is a second crystalline form known as aragonite. These forms convert between themselves according to

\[ \text{Calcite} \leftrightarrow \text{Aragonite} \]

Answer the following using the data provided.

<table>
<thead>
<tr>
<th>Thermodynamic parameter (25 °C)</th>
<th>ΔHƐ</th>
<th>SƐ</th>
<th>ΔGƐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃ (calcite)</td>
<td>-1206.86 kJ/mol</td>
<td>92.88 J/K·mol</td>
<td>-1128.76 kJ/mol</td>
</tr>
<tr>
<td>CaCO₃ (aragonite)</td>
<td>-1207.04 kJ/mol</td>
<td>88.70 J/K·mol</td>
<td>-1127.71 kJ/mol</td>
</tr>
</tbody>
</table>

a) Based on the thermodynamic parameters, would you expect calcite in nature to convert spontaneously to aragonite at 1 atm. and 25 °C? Explain.

We need to know ΔG^\circ for the calcite ↔ aragonite reaction:

\[ \Delta G^\circ = \Delta G^\circ_{ \text{ar} } - \Delta G^\circ_{ \text{calc} } = (-1127.71 \text{ kJ/mol}) - (-1128.76 \text{ kJ/mol}) = +1.05 \text{ kJ/mol} \]

This ΔG^\circ is positive, so the Calcite ↔ Aragonite reaction is not spontaneous at standard state concentrations.

b) At what temperature will calcite and aragonite be at equal (equilibrium) concentrations?

They will be at equilibrium when ΔG = 0. They will be at equal concentrations when ΔG = ΔG^\circ (because ΔG = ΔG^\circ - RT \ln(C_{\text{ar}}/C_{\text{calc}})).

So we need to get T where ΔG^\circ = 0:

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \Rightarrow 0 = -0.18 \frac{\text{kJ}}{\text{mol}} - T \left( -4.18 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \]

\[ 0 = 0.18 \frac{\text{kJ}}{\text{mol}}^{-180 \frac{\text{J}}{\text{mol}}} \text{ mol}^{-1} \]

\[ T = 43.1 \text{ K} = -230 \text{ °C} \]

(I've assumed ΔH^\circ and ΔS^\circ are constant over the T range -30 °C to 25 °C.)
3. The water in freshwater lakes is less salty as compared to the oceans. Consider the oceans to be a 0.5 M NaCl solution and freshwater lakes to be a 0.005 M MgCl₂ solution. For simplicity, consider the salts to be completely dissociated and the solutions sufficiently dilute so that all equations for dilute solutions apply.

a) What is the osmotic pressure of the ocean water at \( T = 300 \text{ K} \)?

\[
\Pi = CRT
\]

Note that NaCl dissociates, so we have
\[
[Na^+] = [Cl^-] = 0.5M
\]

The total concentration of ions dissolved in the ocean is \( 0.5M + 0.5M = 1.0M \)

\[
\Pi = (1.0M)(0.08205 \frac{L \cdot atm}{mol \cdot K})(300K) = 24.6 \text{ atm}
\]

b) What is the osmotic pressure of the lake water at \( T = 300 \text{ K} \)?

Likewise, \( [Mg^{2+}] = 0.005M \) and \( [Cl^-] = 0.01M \)

\[
\Pi = (0.015 \frac{mol}{L})(0.08205 \frac{L \cdot atm}{mol \cdot K})(300K)
\]

\[
= 0.37 \text{ atm}
\]

c) Will water spontaneously transfer from the ocean to lakes or vice versa due to differences in water vapor pressure between the bodies of water? Explain.

It will transfer from the lakes to the ocean spontaneously. The vapor pressure (not osmotic pressure) of a solvent relates to the activity of the solvent by \( \text{Solvent} = \frac{\text{Solvent}}{\text{Solvent pure}} \).

Clearly, the activity of water in the ocean is lower than in the lakes since the mole fraction of H₂O in the ocean is lower than in the ocean. Thus, the water vapor pressure is lower for the ocean compared to the lakes, so H₂O will transfer from lakes to the ocean.
4. Succinate dehydrogenase catalyzes the conversion of succinate into fumarate by the reduction of FAD:

\[ \text{FAD} + \text{COO}'\text{CH}_2\text{CH}_2\text{COO}^- \rightarrow \text{COO}'\text{CHCHCOO}^- + \text{FADH}_2 \]

The reaction is found to follow Michaelis-Menten kinetics, with \( K_M = 0.1 \text{ mM} \).

a) If the initial rate of production of fumarate is found to be 1 mM/min when [succinate] = 0.025 mM and the total concentration of succinate dehydrogenase is 2 \( \mu \text{M} \), what is the value of \( k_{cat} \)?

\[
V_o = \frac{V_{max}}{1 + \frac{K_m}{[S]}}
\]

Let \( V_{max} = k_{cat} [E]_{tot} \)

\[
so \quad V_{max} = V_o \left(1 + \frac{K_m}{[S]}\right)
\]

\[
= \left(1 \text{ mM/min} \right) \left(1 + \frac{0.1 \text{ mM}}{0.025 \text{ mM}}\right) = 8 \text{ mM/min}
\]

\[
\Rightarrow k_{cat} = \frac{V_{max}}{[E]_{tot}} = \frac{8 \text{ mM/min}}{2 \mu \text{M}} = 4000 \text{ min}^{-1}
\]

b) Malonate, COO'CH\_2COO\(^-\), is a competitive reversible inhibitor of succinate dehydrogenase \( K_i \) for malonate = 1 \( \times \) 10\(^{-3} \) M. Under the conditions in part a but when [malonate] = 1 \( \times \) 10\(^{-5} \) M, what will the concentration of succinate when the velocity of production of fumarate is equal to \( V_{max} / 2 \)?

\[
K_{m, app} = K_m \left(1 + \frac{[I]}{K_i}\right) = (0.1 \mu \text{M}) \left(1 + \frac{1 \times 10^{-5} \mu \text{M}}{0.2 \mu \text{M}}\right) = 0.2 \mu \text{M}
\]

\[
V_o = \frac{V_{max}}{2} = \frac{V_{max}}{1 + K_{m, app}/[S]}
\]

\[
\Rightarrow [S] = K_{m, app}/[E]
\]

\[\text{or} \quad [S] = K_{m, app} = 0.2 \mu \text{M} \]

\[\text{or} \quad \alpha = 1 + K_{m, app}/[S] \]

c) What is the concentration of the succinate-enzyme complex (i.e. [ES]) under the conditions in part b with the [succinate] that you found in part b?

This can be solved in a number of ways. One is to note that

\[
V_o = k_{cat} [E][S], \quad \text{so} \quad [ES] = \frac{V_o}{k_{cat}} = \frac{V_{max}/2}{k_{cat} [E]_{tot}/2} = \frac{[E]}{K_m} = \frac{V_{max}/2}{[E]} = \frac{1}{V_{max}/2}
\]

Another is to note that \( K_{m, app} = \frac{[E][S]}{[ES]} \) so \( \frac{[ES]}{[E]} = \frac{K_{m, app}}{[E]} = \frac{0.2 \mu \text{M}}{0.2 \mu \text{M}} = 1. \)

From this \( [E] = [ES] \). We know \( [E]_{tot} = [E] + [ES] \), so \( [E]_{tot} = 2[ES] \)

\[
\text{or} \quad [ES] = \frac{[E]_{tot}}{2} = 0.5 \mu \text{M}
\]

There are other ways to get this besides these two.
5. Tyrosine has a pKₐ for the ionization of the phenolic hydrogen in its side group. The approximate absorption spectra for the protonated and deprotonated forms of tyrosine are

\[ \text{a) Suppose we obtain an absorption spectrum of a peptide that contains 3 tyrosine residues and no tryptophan or phenylalanine. A sample of this peptide in a 1 cm cuvette has an absorbance of 0.3 at 270 nm, 0.5 at 285 nm and 0.2 at 300 nm. What is the total concentration of tyrosine in the cuvette?} \]

\[ A_{285} = (E_{Tyr-OH}C_{Tyr-OH} + E_{Tyr-O}C_{Tyr-O})(1000)(C_{Tyr-O})(1\text{cm}) \]

Thus, the total absorbance at 285 nm can easily tell us the total concentration of tyrosine.

\[ [\text{Tyr}] = 5 \times 10^{-4} \text{M} \]

\[ [\text{Tyr-OH}] = \frac{1}{3} \times [\text{Tyr}] = 1.67 \times 10^{-4} \text{M} \]

\[ [\text{Tyr-O}] = \frac{2}{3} \times [\text{Tyr}] = 3.33 \times 10^{-4} \text{M} \]

\[ \text{We know} \quad [\text{Tyr}] = [\text{Tyr-OH}] + [\text{Tyr-O}] \quad \Rightarrow \quad [\text{Tyr-OH}] = 5 \times 10^{-4} \text{M} - 1.33 \times 10^{-4} \text{M} = 3.67 \times 10^{-4} \text{M} \]

\[ \frac{[\text{Tyr-O}]}{[\text{Tyr-OH}]} = \frac{1.33 \times 10^{-4} \text{M}}{3.67 \times 10^{-4} \text{M}} = 0.362 \]