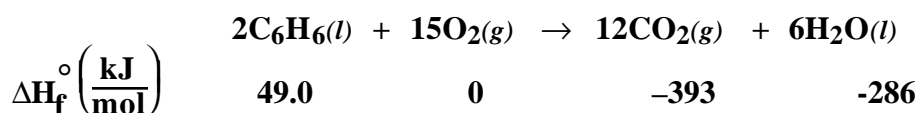
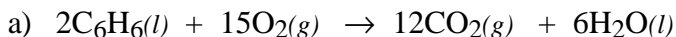
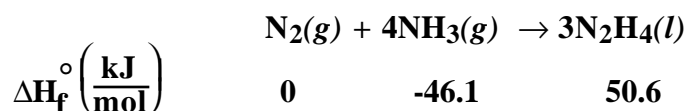
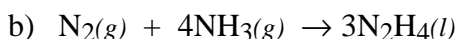


ALL work must be shown in all problems for full credit. **Due by 4:45 pm on Friday, December 7, 2001.**

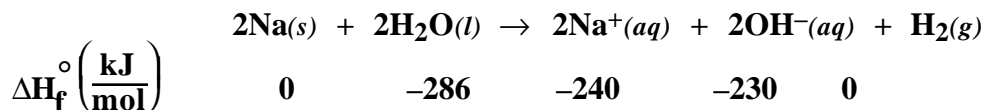
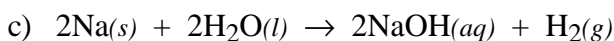
PS15.1. Using the table of thermodynamic values found in Appendix B in your textbook, calculate the $\Delta H^\circ_{\text{rxn}}$ (standard enthalpy change) for each of the following reactions:



$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants}) \\ &= 12\Delta H_f^\circ (\text{CO}_2(g)) + 6\Delta H_f^\circ (\text{H}_2\text{O}(l)) - [2\Delta H_f^\circ (\text{C}_6\text{H}_6(l)) + 15\Delta H_f^\circ (\text{O}_2(g))] \\ &= 12(-393 \text{ kJ}) + 6(-286 \text{ kJ}) - [2(49 \text{ kJ}) + 5(0)] \\ &= -6.53 \times 10^3 \text{ kJ} \end{aligned}$$



$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants}) \\ &= 3\Delta H_f^\circ (\text{N}_2\text{H}_4(l)) - [2\Delta H_f^\circ (\text{N}_2(g)) + 4\Delta H_f^\circ (\text{NH}_3(g))] \\ &= 3(50.6 \text{ kJ}) - [(0 \text{ kJ}) + 4(-46.1)] \\ &= 3.36 \times 10^2 \text{ kJ} \end{aligned}$$



$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants}) \\ &= 2\Delta H_f^\circ (\text{Na}^+(aq)) + 2\Delta H_f^\circ (\text{OH}^-(aq)) + \Delta H_f^\circ (\text{H}_2(g)) - [2\Delta H_f^\circ (\text{Na}(s)) + \\ & 2\Delta H_f^\circ (\text{H}_2\text{O}(l))] \\ &= 2(-240 \text{ kJ}) + 2(-230 \text{ kJ}) + (0 \text{ kJ}) - [2(0 \text{ kJ}) + 2(-286 \text{ kJ})] \\ &= -3.68 \times 10^2 \text{ kJ} \end{aligned}$$

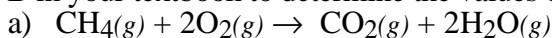
PS15.2. For each of the following pairs, indicate which substance you would expect to possess the larger standard entropy:

- a) 1 mol $\text{H}_2\text{O}(g)$ at 373 K and 1 atm or 1 mol $\text{H}_2\text{O}(l)$ at 373 K and 1 atm.
1 mol $\text{H}_2\text{O}(g)$ at 373 K and 1 atm has greater entropy than 1 mol $\text{H}_2\text{O}(l)$ at 373 K and 1 atm. Molecules of gas have a large amount of space to move about in compared to water molecules in the liquid phase, so there is greater disorder.
- b) 1 mol $\text{NaNO}_3(aq)$ at 30 °C or 1 mol $\text{NaNO}_3(s)$ at 30 °C.
1 mol $\text{NaNO}_3(aq)$ at 30 °C has greater entropy than $\text{NaNO}_3(s)$. Aqueous ions can move more freely in solution, and are more disordered, than the ions in the solid state.
- c) 1 mol $\text{N}_2(g)$ at 10 °C and 1 atm or 1 mol $\text{N}_2(g)$ at 10 °C and 10 atm.
1 mol $\text{N}_2(g)$ at 298 K and 1 atm has greater entropy than at 10 atm. Molecules of gas have a large amount of space to move about in at the lower pressure, so there is greater disorder.
- d) 1 mol $\text{He}(g)$ at 25 °C and 1 atm or 1 mol $\text{N}_2\text{O}(g)$ at 25 °C and 1 atm
1 mol $\text{N}_2\text{O}(g)$ at 25 °C and 1 atm has greater entropy than 1 mol $\text{He}(l)$ at 25 °C. There are more atoms in N_2O compared to He. The molecular complexity of N_2O is much greater than He, so there is greater disorder.

PS15.3. Predict whether the entropy change in the system is positive or negative for each of the following processes: (Note: do not do any calculations.)

- a) $2\text{Hg}(l) + \text{O}_2(g) \rightarrow 2\text{HgO}(s)$ ΔS is –
- b) $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$ ΔS is –
- c) $2\text{KClO}_4(s) \rightarrow 2\text{KClO}_3(s) + \text{O}_2(g)$ ΔS is +
- d) $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$ ΔS is close to 0

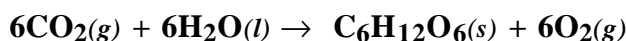
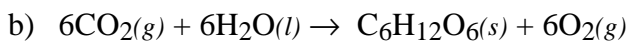
PS15.4. For each reaction below, use the table of thermodynamic values from Appendix B in your textbook to determine the values of ΔH° and ΔS° .



	$\text{CH}_4(g)$	$+ 2\text{O}_2(g)$	\rightarrow	$\text{CO}_2(g)$	$+ 2\text{H}_2\text{O}(g)$
$\Delta H_f^\circ \left(\frac{\text{kJ}}{\text{mol}} \right)$	-75	0		-393.5	-242
$S^\circ \left(\frac{\text{J}}{\text{K}\cdot\text{mol}} \right)$	186	205		214	189

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) \\ &= \Delta H_f^\circ (\text{CO}_2(g)) + 2\Delta H_f^\circ (\text{H}_2\text{O}(g)) - [\Delta H_f^\circ (\text{CH}_4(g)) + 2\Delta H_f^\circ (\text{O}_2(g))] \\ &= (-393.5 \text{ kJ}) + (-242 \text{ kJ}) - [(-75 \text{ kJ}) + (0)] \\ &= -802 \text{ kJ} \end{aligned}$$

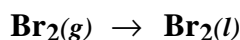
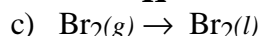
$$\begin{aligned} \Delta S_{\text{rxn}}^\circ &= \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants}) \\ &= S^\circ (\text{CO}_2(g)) + 2S^\circ (\text{H}_2\text{O}(g)) - [S^\circ (\text{CH}_4(g)) + 2S^\circ (\text{O}_2(g))] \\ &= \left[\left(214 \frac{\text{J}}{\text{K}} \right) + \left(189 \frac{\text{J}}{\text{K}} \right) \right] - \left[\left(186 \frac{\text{J}}{\text{K}} \right) + \left(205 \frac{\text{J}}{\text{K}} \right) \right] = -4 \text{ J/K} \end{aligned}$$



$\Delta\text{H}_f^\circ \left(\frac{\text{kJ}}{\text{mol}} \right)$	-393.5	-285	-1273	0
$\text{S}^\circ \left(\frac{\text{J}}{\text{K}\cdot\text{mol}} \right)$	214	70	212	205

$$\begin{aligned} \Delta\text{H}_{\text{rxn}} &= \sum \Delta\text{H}_f^\circ (\text{products}) - \sum \Delta\text{H}_f^\circ (\text{reactants}) \\ &= [\Delta\text{H}_f^\circ (\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6\Delta\text{H}_f^\circ (\text{O}_2(\text{g}))] - [6\Delta\text{H}_f^\circ (\text{CO}_2(\text{g})) + 6\Delta\text{H}_f^\circ (\text{H}_2\text{O}(\text{l}))] \\ &= (-1273 \text{ kJ}) + 6(0 \text{ kJ}) - [6(-393.5 \text{ kJ}) + 6(-285 \text{ kJ})] \\ &= 2798 \text{ kJ} \end{aligned}$$

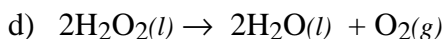
$$\begin{aligned} \Delta\text{S}_{\text{rxn}} &= \sum \text{S}^\circ (\text{products}) - \sum \text{S}^\circ (\text{reactants}) \\ &= [\text{S}^\circ (\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6\text{S}^\circ (\text{O}_2(\text{g}))] - [6\text{S}^\circ (\text{CO}_2(\text{g})) + 6\text{S}^\circ (\text{H}_2\text{O}(\text{l}))] \\ &= \left[\left(212 \frac{\text{J}}{\text{K}} \right) + 6 \left(205 \frac{\text{J}}{\text{K}} \right) \right] - \left[6 \left(214 \frac{\text{J}}{\text{K}} \right) + 6 \left(70 \frac{\text{J}}{\text{K}} \right) \right] = -262 \text{ J/K} \end{aligned}$$



$\Delta\text{H}_f^\circ \left(\frac{\text{kJ}}{\text{mol}} \right)$	30.9	0
$\text{S}^\circ \left(\frac{\text{J}}{\text{K}\cdot\text{mol}} \right)$	245	152

$$\begin{aligned} \Delta\text{H}_{\text{rxn}} &= \sum \Delta\text{H}_f^\circ (\text{products}) - \sum \Delta\text{H}_f^\circ (\text{reactants}) \\ &= \Delta\text{H}_f^\circ (\text{Br}_2(\text{l})) - [\Delta\text{H}_f^\circ (\text{Br}_2(\text{g}))] = (0 \text{ kJ}) - [(30.9 \text{ kJ})] = -30.9 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta\text{S}_{\text{rxn}} &= \sum \text{S}^\circ (\text{products}) - \sum \text{S}^\circ (\text{reactants}) \\ &= \text{S}^\circ (\text{Br}_2(\text{l})) - [\text{S}^\circ (\text{Br}_2(\text{g}))] \\ &= \left[\left(152 \frac{\text{J}}{\text{K}} \right) \right] - \left[\left(245 \frac{\text{J}}{\text{K}} \right) \right] = -93 \frac{\text{J}}{\text{K}} \end{aligned}$$



$\Delta\text{H}_f^\circ \left(\frac{\text{kJ}}{\text{mol}} \right)$	-188	-286	0
$\text{S}^\circ \left(\frac{\text{J}}{\text{K}\cdot\text{mol}} \right)$	110	70	205

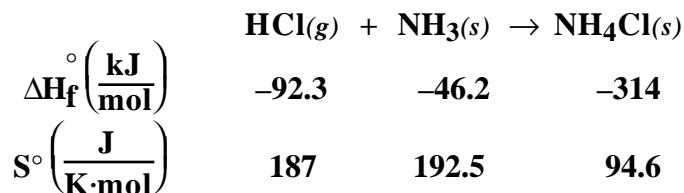
$$\begin{aligned} \Delta\text{H}_{\text{rxn}} &= \sum \Delta\text{H}_f^\circ (\text{products}) - \sum \Delta\text{H}_f^\circ (\text{reactants}) \\ &= 2\Delta\text{H}_f^\circ (\text{H}_2\text{O}(\text{l})) + \Delta\text{H}_f^\circ (\text{O}_2(\text{g})) - [2\Delta\text{H}_f^\circ (\text{H}_2\text{O}_2(\text{l}))] \\ &= 2(-286 \text{ kJ}) + (0 \text{ kJ}) - [2(-188 \text{ kJ})] = -196 \text{ kJ} \end{aligned}$$

$$\Delta\text{S}_{\text{rxn}} = \sum \text{S}^\circ (\text{products}) - \sum \text{S}^\circ (\text{reactants})$$

$$= 2S^\circ(\text{H}_2\text{O}(l)) + S^\circ(\text{O}_2(g)) - [2S^\circ(\text{H}_2\text{O}_2(l))]]$$

$$= [2(70 \frac{\text{J}}{\text{K}}) + (205 \frac{\text{J}}{\text{K}})] - [2(110 \frac{\text{J}}{\text{K}})] = +125 \frac{\text{J}}{\text{K}}$$

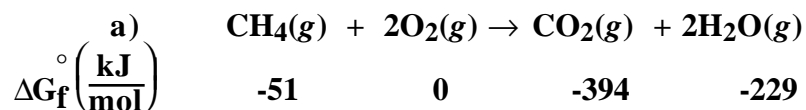
e) $\text{HCl}(g) + \text{NH}_3(g) \rightarrow \text{NH}_4\text{Cl}(s)$



$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) = -175.5 \text{ kJ}$$

$$\Delta S_{\text{rxn}}^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants}) = -285 \frac{\text{J}}{\text{K}}$$

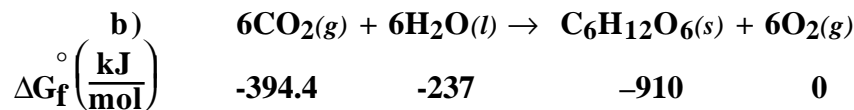
PS15.5. a) Calculate ΔG° for each of the reactions in problem PS15.4.



$$\Delta G_{\text{rxn}}^\circ = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants})$$

$$= \Delta G_f^\circ (\text{CO}) + 2\Delta G_f^\circ (\text{H}_2\text{O}) - [\Delta G_f^\circ (\text{CH}_4) + 2\Delta G_f^\circ (\text{O})]$$

$$= (-394 \text{ kJ}) + 2(-229 \text{ kJ}) - [(-51 \text{ kJ}) + 2(0)] = -801 \text{ kJ}$$

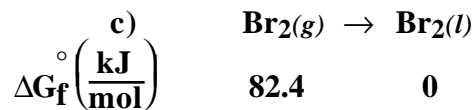


$$\Delta G_{\text{rxn}}^\circ = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants})$$

$$= [\Delta G_f^\circ (\text{C}_6\text{H}_{12}\text{O}_6(s)) + 6\Delta G_f^\circ (\text{O}_2(g))] - 6\Delta G_f^\circ (\text{CO}_2(g)) + 6\Delta G_f^\circ (\text{H}_2\text{O}(l))$$

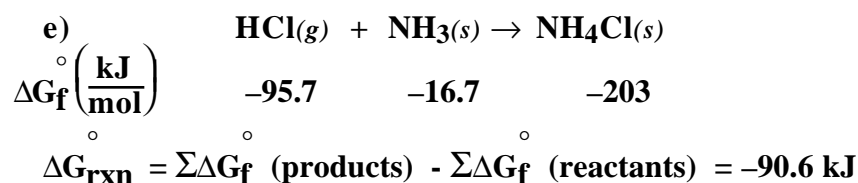
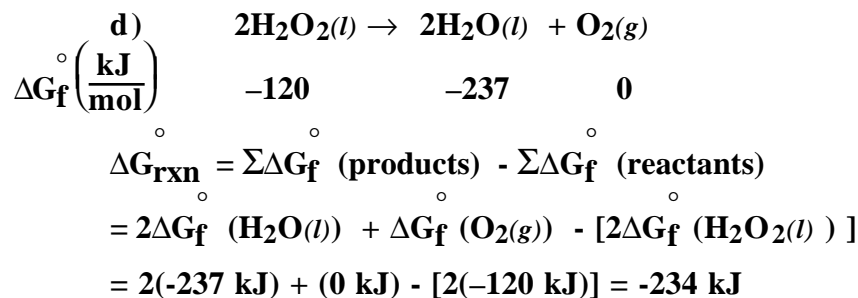
$$= (-910 \text{ kJ}) + 6(0 \text{ kJ}) - [6(-394.4 \text{ kJ}) + 6(-237 \text{ kJ})]$$

$$= 2878 \text{ kJ}$$



$$\Delta G_{\text{rxn}}^\circ = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants})$$

$$= \Delta G_f^\circ (\text{Br}_2(l)) - [\Delta G_f^\circ (\text{Br}_2(g))] = (0 \text{ kJ}) - [(3.11 \text{ kJ})] = -3.11 \text{ kJ}$$



b) Which of the reactions in PS14.4 are spontaneous at 298 K?

a), c), d) and e).

c) For each of the reactions listed in b), find the temperature above or below which the reaction becomes nonspontaneous.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

when ΔG° is zero, then,

$$0 = \Delta H^\circ - T\Delta S^\circ$$

and

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

In 4a):

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-802 \text{ kJ}}{-4 \times 10^{-3} \frac{\text{kJ}}{\text{K}}} = 2.01 \times 10^5 \text{ K}$$

If the temperature is greater than $2.01 \times 10^5 \text{ K}$ the reaction will be nonspontaneous!

In 4c):

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-30.9 \text{ kJ}}{-0.093 \frac{\text{kJ}}{\text{K}}} = 332 \text{ K}$$

If the temperature is greater than 332 K the reaction will be nonspontaneous!

In 4d):

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-196 \text{ kJ}}{0.125 \frac{\text{kJ}}{\text{K}}} = -1568 \text{ K}$$

The temperature can never be less than 0 K, so reaction is spontaneous at all temperatures!

In 4e):

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-175.5 \text{ kJ}}{-0.285 \frac{\text{kJ}}{\text{K}}} = 616 \text{ K}$$

If the temperature is greater than 616 K the reaction will be nonspontaneous!

d) Which of the reactions in PS14.4 are nonspontaneous at 298 K?

b)

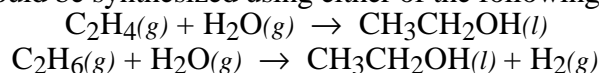
e) For each of the reactions listed in d), find the temperature above or below which the reaction becomes spontaneous.

In 4b):

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{2798 \text{ kJ}}{-0.262 \frac{\text{kJ}}{\text{K}}} = -1.07 \times 10^4 \text{ K}$$

The temperature can never be less than 0 K, so reaction is nonspontaneous at all temperatures!

PS15.6. Ethanol could be synthesized using either of the following reactions;



Using thermodynamics arguments which reaction is more feasible under standard conditions? Explain.

$$\begin{array}{cccc} \Delta G_f^\circ \left(\frac{\text{kJ}}{\text{mol}} \right) & 68.1 & -228.6 & -174.8 \\ \text{C}_2\text{H}_4(g) + \text{H}_2\text{O}(g) & \rightarrow & \text{CH}_3\text{CH}_2\text{OH}(l) & \\ \Delta G_{\text{rxn}}^\circ & = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants}) & & \\ & = \Delta G_f^\circ (\text{CH}_3\text{CH}_2\text{OH}(l)) - [\Delta G_f^\circ (\text{C}_2\text{H}_4(g)) + \Delta G_f^\circ (\text{H}_2\text{O}(g))] & & \\ & = (-174.8 \text{ kJ}) - [(68.1 \text{ kJ}) + (-228.6)] = -14.3 \text{ kJ} & & \end{array}$$

$$\begin{array}{cccccc} \Delta G_f^\circ \left(\frac{\text{kJ}}{\text{mol}} \right) & -32.9 & -228.6 & -174.8 & 0 & \\ \text{C}_2\text{H}_6(g) + \text{H}_2\text{O}(g) & \rightarrow & \text{CH}_3\text{CH}_2\text{OH}(l) + \text{H}_2(g) & & & \\ \Delta G_{\text{rxn}}^\circ & = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants}) & & & & \\ & = \Delta G_f^\circ (\text{CH}_3\text{CH}_2\text{OH}(l)) + \Delta G_f^\circ (\text{H}_2) - [\Delta G_f^\circ (\text{C}_2\text{H}_6(g)) + \Delta G_f^\circ (\text{H}_2\text{O}(g))] & & & & \\ & = (-174.8 \text{ kJ}) + (0 \text{ kJ}) - [(-32.9 \text{ kJ}) + (-228.6)] = 86.7 \text{ kJ} & & & & \end{array}$$

The first reaction between water and ethylene is spontaneous (feasible) while the other reaction is nonspontaneous.

PS15.7. When liquid water is introduced into an evacuated vessel at 25 °C, some of the water vaporizes. Predict how the enthalpy, entropy, and free energy change in the system during this process. Explain the reasoning behind your predictions.

ΔH° is positive for the conversion of water in the liquid phase to water in the gas phase. Heat must be added to convert a liquid into a gas.

ΔS° is positive because the gas phase is more disordered compared to the liquid phase.

ΔG° is negative because under the nonstandard conditions of an evacuated vessel, some liquid must vaporize to reach the equilibrium vapor pressure at 25 °C.

PS15.8. Under what conditions do enthalpy, entropy and free energy take on values of zero?

Enthalpy

ΔH_f° is zero for elements in their standard state.

when ΔH_{rxn}° is zero no heat is released or absorbed in the reaction.

Entropy

S° is zero for pure solids at 0 Kelvin.

when ΔS_{rxn}° is zero the disorder of the reaction does not change.

Free energy

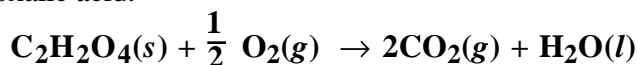
ΔG_{rxn} is zero when the reaction is at equilibrium

ΔG_f° is zero for elements in their standard state.

PS15.9. The enthalpy of combustion, ΔH°_{comb} , for oxalic acid, $C_2H_2O_4(s)$, is $-246.05 \text{ kJ}\cdot\text{mol}^{-1}$ and

Substance	$\Delta H_f^\circ \left(\frac{\text{kJ}}{\text{mol}} \right)$	$S^\circ \left(\frac{\text{J}}{\text{mol}\cdot\text{K}} \right)$
$C(s)$	0	5.69
$CO_2(g)$	-393.5	213.6
$H_2(g)$	0	130.6
$H_2O(l)$	-285.8	69.96
$O_2(g)$	0	205
$C_2H_2O_4(s)$?	120.1

a) Write the balanced chemical equation that describes the combustion of one mole of oxalic acid.



b) Write the balanced chemical equation which describes the standard formation of oxalic acid.



c) Using the information given above and the equations in a) and b), calculate ΔH_f° for oxalic acid.

$$\begin{aligned} \Delta H_{comb}^\circ &= \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactant}) \\ &= 2\Delta H_f^\circ (CO_2) + \Delta H_f^\circ (H_2O) - [\Delta H_f^\circ (C_2H_2O_4) + \frac{1}{2} \Delta H_f^\circ (O_2)] \\ -246.05 \frac{\text{kJ}}{\text{mol}} &= 2(-393.5 \frac{\text{kJ}}{\text{mol}} + (-285.8 \frac{\text{kJ}}{\text{mol}}) - [(C_2H_2O_4 + \frac{1}{2}(0 \frac{\text{kJ}}{\text{mol}})] \\ \Delta H_f^\circ [C_2H_2O_4] &= -826.8 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

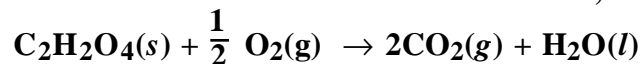
d) Calculate ΔS_f° for oxalic acid and ΔS°_{rxn} for the combustion of one mole of oxalic acid.

The formation reaction for oxalic acid is,



$$\begin{aligned} \Delta S_f^\circ &= \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants}) \\ &= S^\circ(C_2H_2O_4) - [2S^\circ(C) + S^\circ(H_2) + 2S^\circ(O_2)] \\ &= 120.1 \frac{\text{J}}{\text{K}} - [2(5.69 \frac{\text{J}}{\text{K}}) + (130.6 \frac{\text{J}}{\text{K}}) + 2(205 \frac{\text{J}}{\text{K}})] = -431.9 \frac{\text{J}}{\text{K}} \end{aligned}$$

The combustion reaction for oxalic acid is,



$$\begin{aligned}\Delta S_{\text{comb}}^{\circ} &= \sum S^{\circ}(\text{products}) - \sum S^{\circ}(\text{reactants}) \\ &= 2S^{\circ}(\text{CO}_2) + S^{\circ}(\text{H}_2\text{O}) - [S^{\circ}(\text{C}_2\text{H}_2\text{O}_4) + \frac{1}{2} S^{\circ}(\text{O}_2)] \\ &= 2\left(213.6 \frac{\text{J}}{\text{K}}\right) + (69.96 \frac{\text{J}}{\text{K}}) - \left[\left(120.1 \frac{\text{J}}{\text{K}}\right) + \frac{1}{2} \left(205 \frac{\text{J}}{\text{K}}\right)\right] = 274.6 \frac{\text{J}}{\text{K}}\end{aligned}$$

- e) Calculate ΔG_f° for oxalic acid and $\Delta G_{\text{rxn}}^{\circ}$ for the combustion of one mole of oxalic acid.

$$\Delta G_f^{\circ} = \Delta H_f^{\circ} - T\Delta S_f^{\circ}$$
$$\Delta G_f^{\circ} = -826.8 \frac{\text{kJ}}{\text{mol}} - 298 \text{ K} \left(-0.4319 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \right) = -698.1 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G^{\circ}_{\text{comb}} = \Delta H^{\circ}_{\text{comb}} - T\Delta S^{\circ}_{\text{comb}}$$
$$\Delta G^{\circ}_{\text{comb}} = -246.05 \frac{\text{kJ}}{\text{mol}} - 298 \text{ K} \left(0.2746 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \right) = -327.9 \frac{\text{kJ}}{\text{mol}}$$

- f) Is the formation of oxalic acid from its elements spontaneous? Is the combustion of oxalic acid at 25 °C spontaneous?

The formation of oxalic acid is spontaneous. The combustion of oxalic acid is spontaneous.