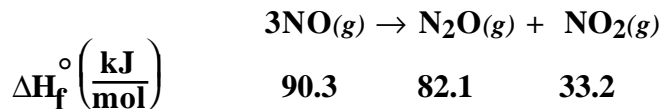
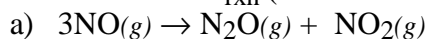
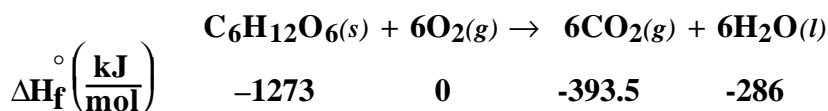
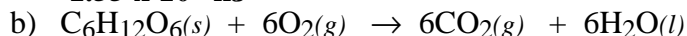


ALL work must be shown to receive full credit. **Due in lecture, at 8:30 a.m. on Friday, January 25, 2002.**

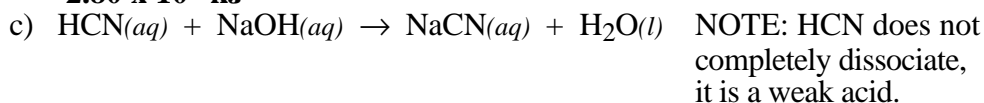
PS1.1. Using the table of thermodynamic values found in Appendix B in your textbook, calculate the  $\Delta H^\circ_{\text{rxn}}$  (standard enthalpy change) for each of the following reactions:



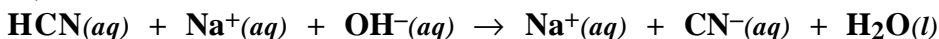
$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) \\ &= [\Delta H_f^\circ (\text{N}_2\text{O}(g)) + \Delta H_f^\circ (\text{NO}_2(g))] - 3\Delta H_f^\circ (\text{NO}(g)) \\ &= [(82.1 \text{ kJ}) + (33.2)] - 3(90.3 \text{ kJ}) \\ &= -1.55 \times 10^2 \text{ kJ} \end{aligned}$$



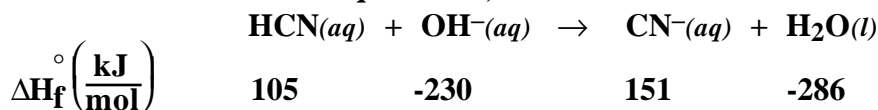
$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) \\ &= [6\Delta H_f^\circ (\text{CO}_2(g)) + 6\Delta H_f^\circ (\text{H}_2\text{O}(l))] - [\Delta H_f^\circ (\text{C}_6\text{H}_{12}\text{O}_6(s)) + 6\Delta H_f^\circ (\text{O}_2(g))] \\ &= [6(-393.5 \text{ kJ}) + 6(-286 \text{ kJ})] - [(-1273 \text{ kJ}) + 6(0 \text{ kJ})] \\ &= -2.80 \times 10^3 \text{ kJ} \end{aligned}$$



We need to write this equation as a net ionic equation, the ionic equation is,



The net ionic equation is,



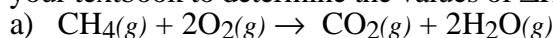
$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants}) \\ &= [\Delta H_f^\circ (\text{CN}^-(aq)) + \Delta H_f^\circ (\text{H}_2\text{O}(l))] - [\Delta H_f^\circ (\text{HCN}(aq)) + \Delta H_f^\circ (\text{OH}^-(aq))] \\ &= [(151 \text{ kJ}) + (-286 \text{ kJ})] - [(105 \text{ kJ}) + (-230 \text{ kJ})] \\ &= -10 \text{ kJ} \end{aligned}$$

- PS1.2. For each of the following pairs, indicate which substance you would expect to possess the larger standard entropy. In each case provide a short explanation.
- 1 mol  $\text{CH}_3\text{OH}(g)$  at 373 K and 1 atm or 1 mol  $\text{CH}_3\text{OH}(l)$  at 373 K and 1 atm.  
**1 mol  $\text{CH}_3\text{OH}(g)$  at 373 K and 1 atm has greater entropy than 1 mol  $\text{CH}_3\text{OH}(l)$  at 373 K and 1 atm. Molecules of gas have a large amount of space to move about in compared to molecules in the liquid phase, so there is greater disorder in the gas phase.**
  - 1 mol  $\text{Na}_2\text{SO}_4(aq)$  at 23 °C or 1 mol  $\text{Na}_2\text{SO}_4(s)$  at 23 °C.  
**1 mol  $\text{Na}_2\text{SO}_4(aq)$  at 30 °C has greater entropy than  $\text{Na}_2\text{SO}_4(s)$ . Aqueous ions can move more freely in solution, can take on many more possible positions and are more disordered. In the solid state the ions are in fixed positions and are unable to move.**
  - 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.**
  - 1 mol  $\text{He}(g)$  at 25 °C and 1 atm or 1 mol  $\text{C}_2\text{Cl}_6(g)$  at 25 °C and 1 atm  
**1 mol  $\text{C}_2\text{Cl}_6(g)$  at 25 °C and 1 atm has greater entropy than 1 mol  $\text{He}(l)$  at 25 °C. There are more atoms in  $\text{C}_2\text{Cl}_6$  compared to He. The molecular complexity of  $\text{C}_2\text{Cl}_6$  is much greater than He, so there is greater disorder.**

PS1.3. Predict whether the entropy change in the system is positive or negative for each of the following processes: (Note: do not do any calculations.)

- $8\text{H}_2\text{S}(g) + 4\text{O}_2(g) \rightarrow \text{S}_8(s) + 8\text{H}_2\text{O}(g)$   $\Delta S$  is –
- $2\text{K}(s) + \text{F}_2(g) \rightarrow 2\text{KF}(s)$   $\Delta S$  is –
- $\text{CaCO}_3(s) + 2\text{HCl}(aq) \rightarrow 2\text{CaCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$   $\Delta S$  is +
- $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$   $\Delta S$  is close to 0

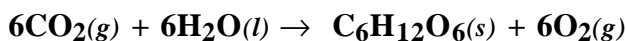
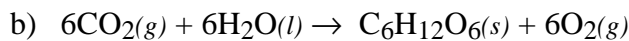
PS1.4. For each reaction below, use the table of thermodynamic values from Appendix B in your textbook to determine the values of  $\Delta H^\circ$  and  $\Delta S^\circ$ .



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

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

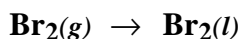
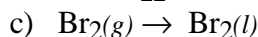
$$\begin{aligned} \Delta S_{\text{rxn}}^\circ &= \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants}) \\ &= S^\circ (\text{CO}_2(g)) + 2S^\circ (\text{H}_2\text{O}(g)) - [S^\circ (\text{CH}_4(g)) + 2S^\circ (\text{O}_2(g))] \\ &= \left[ \left( 214 \frac{\text{J}}{\text{K}} \right) + \left(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



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

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

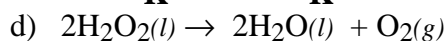
$$\begin{aligned} \Delta\text{S}_{\text{rxn}} &= \sum \text{S}^\circ (\text{products}) - \sum \text{S}^\circ (\text{reactants}) \\ &= [\text{S}^\circ (\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6\text{S}^\circ (\text{O}_2(\text{g}))] - [6\text{S}^\circ (\text{CO}_2(\text{g})) + 6\text{S}^\circ (\text{H}_2\text{O}(\text{l}))]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



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

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

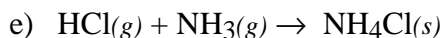
$$\begin{aligned} \Delta\text{S}_{\text{rxn}} &= \sum \text{S}^\circ (\text{products}) - \sum \text{S}^\circ (\text{reactants}) \\ &= \text{S}^\circ (\text{Br}_2(\text{l})) - [\text{S}^\circ (\text{Br}_2(\text{g}))] \\ &= \left[ \left( 152 \frac{\text{J}}{\text{K}} \right) \right] - \left[ \left( 245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



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

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

$$\begin{aligned} \Delta\text{S}_{\text{rxn}} &= \sum \text{S}^\circ (\text{products}) - \sum \text{S}^\circ (\text{reactants}) \\ &= 2\text{S}^\circ (\text{H}_2\text{O}(\text{l})) + \text{S}^\circ (\text{O}_2(\text{g})) - [2\text{S}^\circ (\text{H}_2\text{O}_2(\text{l}))] \\ &= \left[ 2 \left( 70 \frac{\text{J}}{\text{K}} \right) + \left( 205 \frac{\text{J}}{\text{K}} \right) \right] - \left[ 2 \left( 110 \frac{\text{J}}{\text{K}} \right) \right] = +125 \frac{\text{J}}{\text{K}} \end{aligned}$$



	$\text{HCl}(g)$	$+ \text{NH}_3(g)$	$\rightarrow \text{NH}_4\text{Cl}(s)$
$\Delta H_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	-92.3	-46.2	-314
$S^\circ \left( \frac{\text{J}}{\text{K}\cdot\text{mol}} \right)$	187	192.5	94.6

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

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

PS1.5. a) Calculate  $\Delta G^\circ$  for each of the reactions in problem PS1.4.

a)  $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$

$\Delta G_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	-51	0	-394	-229
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$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants}) \\ &= \Delta G_f^\circ (\text{CO}) + 2\Delta G_f^\circ (\text{H}_2\text{O}) - [\Delta G_f^\circ (\text{CH}_4) + 2\Delta G_f^\circ (\text{O})] \\ &= (-394 \text{ kJ}) + 2(-229 \text{ kJ}) - [(-51 \text{ kJ}) + 2(0)] = -801 \text{ kJ} \end{aligned}$$

b)  $6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g)$

$\Delta G_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	-394.4	-237	-910	0
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$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants}) \\ &= [\Delta G_f^\circ (\text{C}_6\text{H}_{12}\text{O}_6(s)) + 6\Delta G_f^\circ (\text{O}_2(g))] - 6\Delta G_f^\circ (\text{CO}_2(g)) + 6\Delta G_f^\circ (\text{H}_2\text{O}(l)) \\ &= (-910 \text{ kJ}) + 6(0 \text{ kJ}) - [6(-394.4 \text{ kJ}) + 6(-237 \text{ kJ})] \\ &= 2878 \text{ kJ} \end{aligned}$$

c)  $\text{Br}_2(g) \rightarrow \text{Br}_2(l)$

$\Delta G_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	82.4	0
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$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants}) \\ &= \Delta G_f^\circ (\text{Br}_2(l)) - [\Delta G_f^\circ (\text{Br}_2(g))] = (0 \text{ kJ}) - [(3.11 \text{ kJ})] = -3.11 \text{ kJ} \end{aligned}$$

d)  $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$

$\Delta G_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	-120	-237	0
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$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants}) \\ &= 2\Delta G_f^\circ (\text{H}_2\text{O}(l)) + \Delta G_f^\circ (\text{O}_2(g)) - [2\Delta G_f^\circ (\text{H}_2\text{O}_2(l))] \\ &= 2(-237 \text{ kJ}) + (0 \text{ kJ}) - [2(-120 \text{ kJ})] = -234 \text{ kJ} \end{aligned}$$

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

$\Delta G_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	-95.7	-16.7	-203
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$$\Delta G_{\text{rxn}}^{\circ} = \sum \Delta G_{\text{f}}^{\circ} (\text{products}) - \sum \Delta G_{\text{f}}^{\circ} (\text{reactants}) = -90.6 \text{ kJ}$$

b) Which of the reactions in PS1.4 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  $\Delta G^{\circ}$  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 PS1.4 are nonspontaneous at 298 K?

b)

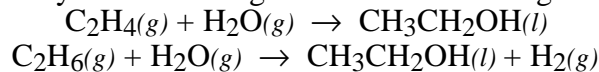
e) For each of the reactions listed in d), find the temperature above or below which the reaction becomes spontaneous.

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!

PS1.6. Ethanol could be synthesized using either of the following reactions;



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

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

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

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

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

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

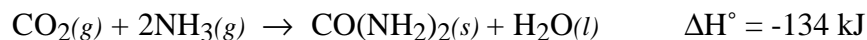
PS1.7. When liquid water is introduced into an evacuated vessel at 25 °C, some of the water vaporizes. Predict how the enthalpy, entropy, and free energy change in the system during this process. Explain the reasoning behind your predictions.

$\Delta H^\circ$  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.

$\Delta S^\circ$  is positive because the gas phase is more disordered compared to the liquid phase.

$\Delta G^\circ$  is negative because under the nonstandard conditions of an evacuated vessel, some liquid must vaporize to reach the equilibrium vapor pressure at 25 °C.

PS1.8. Consider the reaction represented below, which is spontaneous at 298 K.



- a) For the reaction, indicate whether the standard entropy change,  $\Delta S^\circ_{\text{rxn}}$  is positive, negative or zero. Justify your answer. (NOTE: do not use a calculation to justify your answer.)

**$\Delta S$  for this reaction is  $-$ . Three moles of gases form a mol of solid and a mol of liquid. So there are two issues here;**

- 1) three moles of reactant particles forming two moles of product particles. Since there are fewer molecules for all of the atoms to be distributed into the products are more ordered than the reactants;**
- 2) gases converted to a solid and a liquid. Solids are more ordered than liquids are more ordered than gases. Again the products are more ordered compared to the reactants.**

**It should be noted that the comparison of the phases is more important than the number of particles when predicting the  $\Delta S$  (qualitatively). In this case both contribute to the increased order in the products. If these two contributions are opposed, the phase contribution always defines  $\Delta S$ . It is important to site both contributions in your argument/explanation, but the sign of  $\Delta S$  depends on the phase change first. If the same phase in the reactants and products, use the different number of moles to predict. If both phase and moles are the same, molecular complexity becomes the deciding factor. This latter contribution occurs in PS1.3d. NO is more complex compared to N<sub>2</sub> or O<sub>2</sub>.**

- b) Which factor, the change in enthalpy,  $\Delta H^\circ$ , or the change in entropy,  $\Delta S^\circ$ , provides the principal driving force for the reaction at 298 K? Explain.

**Since the reaction is spontaneous, and entropy is not favoring spontaneity,  $\Delta H$  has to be the driving force.  $\Delta H$  is very negative, the reaction is very exothermic**

- c) For the reaction, how is the value of the standard free energy change,  $\Delta G^\circ$ , affected by an increase in temperature? Explain.

**Using the Gibbs-Helmholtz equation,**

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

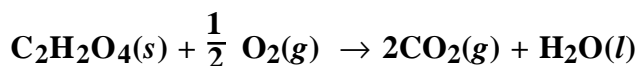
**Since  $\Delta H$  is  $-$  and  $\Delta S$  is  $-$ ,  $\Delta G$  will become less negative (less spontaneous) with increasing temperature.**

$$\Delta G = (-) - T(-)$$

PS1.9. The enthalpy of combustion,  $\Delta H^\circ_{\text{comb}}$ , for oxalic acid,  $\text{C}_2\text{H}_2\text{O}_4(s)$ , is  $-246.05 \text{ kJ}\cdot\text{mol}^{-1}$  and

Substance	$\Delta H^\circ_f \left( \frac{\text{kJ}}{\text{mol}} \right)$	$S^\circ \left( \frac{\text{J}}{\text{mol}\cdot\text{K}} \right)$
$\text{C}(s)$	0	5.69
$\text{CO}_2(g)$	-393.5	213.6
$\text{H}_2(g)$	0	130.6
$\text{H}_2\text{O}(l)$	-285.8	69.96
$\text{O}_2(g)$	0	205
$\text{C}_2\text{H}_2\text{O}_4(s)$	?	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.

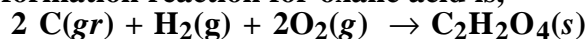


c) Using the information given above and the equations in a) and b), calculate  $\Delta H^\circ_f$  for oxalic acid.

$$\begin{aligned} \Delta H^\circ_{\text{comb}} &= \sum \Delta H^\circ_f (\text{products}) - \sum \Delta H^\circ_f (\text{reactant}) \\ &= 2\Delta H^\circ_f (\text{CO}_2) + \Delta H^\circ_f (\text{H}_2\text{O}) - [\Delta H^\circ_f (\text{C}_2\text{H}_2\text{O}_4) + \frac{1}{2} \Delta H^\circ_f (\text{O}_2)] \\ -246.05 \frac{\text{kJ}}{\text{mol}} &= 2(-393.5 \frac{\text{kJ}}{\text{mol}} + (-285.8 \frac{\text{kJ}}{\text{mol}}) - [(\text{C}_2\text{H}_2\text{O}_4 + \frac{1}{2} (0 \frac{\text{kJ}}{\text{mol}}) ] \\ \Delta H^\circ_f [\text{C}_2\text{H}_2\text{O}_4] &= -826.8 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

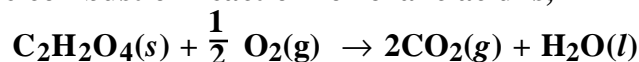
d) Calculate  $\Delta S^\circ_f$  for oxalic acid and  $\Delta S^\circ_{\text{rxn}}$  for the combustion of one mole of oxalic acid.

The formation reaction for oxalic acid is,



$$\begin{aligned} \Delta S^\circ_f &= \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants}) \\ &= S^\circ(\text{C}_2\text{H}_2\text{O}_4) - [2S^\circ(\text{C}) + S^\circ(\text{H}_2) + 2S^\circ(\text{O}_2)] \\ &= 120.1 \frac{\text{J}}{\text{K}} - [2(5.69 \frac{\text{J}}{\text{K}}) + (130.6 \frac{\text{J}}{\text{K}}) + 2(205 \frac{\text{J}}{\text{K}})] = -431.9 \frac{\text{J}}{\text{K}} \end{aligned}$$

The combustion reaction for oxalic acid is,



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

e) Calculate  $\Delta G^\circ_f$  for oxalic acid and  $\Delta G^\circ_{\text{rxn}}$  for the combustion of one mole of oxalic acid.

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



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

$$\Delta G^\circ_{\text{comb}} = \Delta H^\circ_{\text{comb}} - T\Delta S^\circ_{\text{comb}}$$

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

- 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.**