

Types of Thermodynamics Problems

1. Comparing Entropy Values

a) Predict which substance in each pair has the higher entropy. Assume there is one mole of each substance at 25°C and 1 atm.

- i. Hg(l) or CO(g)
gas particles are in much more random motion than liquid particles
- ii. CH₃OH(l) or CH₃CH₂OH(l)
CH₃CH₂OH is a larger, more complex molecule, thus it has a larger number of ways to distribute E.
- iii. KI(s) or CaS(s)
The attractive forces between K⁺ and I⁻ ions are weaker causing more vibrational movement, thus higher entropy.
- iv. CO₂(s) or CO₂(g)
gas particles are in much more random motion than solid particles.

b) Predict which substance has the higher entropy, assume there is one mole of each substance at 25°C: N₂(g) at 1 atm or N₂(g) at 1.0 x 10⁻² atm.

Gases at lower pressures occupy a greater volume. With a greater volume, the number of ways to distribute E increases. Thus entropy of a gas increases as pressure decreases.

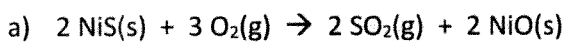
2. Predicting the Sign of ΔS

Predict the sign of the entropy change for each of the following processes. $\Delta S = S_{\text{final}} - S_{\text{initial}}$

- a) Solid sugar is added to water to form a solution.
 ΔS is positive since the sugar molecules become more randomly dispersed in the water, thus entropy increases.
- b) Iodine vapor condenses on a cold surface to form crystals.
 ΔS is negative since solids have less entropy than gases, thus entropy decreases.
- c) $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$
 ΔS is negative. 3 mol gas \rightarrow 2 mol gas. Entropy decreases.
- d) $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$
 ΔS is positive. 9 mol gas \rightarrow 10 mol gas. Entropy increases.
- e) $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$
 ΔS is negative. Solids have less entropy than liquids. Entropy decreases.

3. Calculating ΔS° from S° $\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$

Calculate ΔS° at 25°C using S° data (Appendix 4) for each reaction.

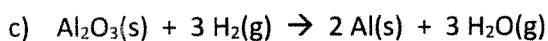


$$\Delta S^\circ = [(2)(248 \text{ J/mol}\cdot\text{K}) + (2)(38 \text{ J/mol}\cdot\text{K})] - [(2)(53 \text{ J/mol}\cdot\text{K}) + (3)(205 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = [572 \text{ J/mol}\cdot\text{K}] - [721 \text{ J/mol}\cdot\text{K}] = \boxed{-149 \text{ J/mol}\cdot\text{K}}$$

b) Using the balanced equation and ΔS° in (a), calculate ΔS° when 4.2 mol of NiS(s) react.

$$\frac{4.2 \text{ mol NiS}}{2 \text{ mol NiS}} \left| \frac{-149 \text{ J}}{2 \text{ mol NiS}} \right. = -312.9 \text{ J}$$

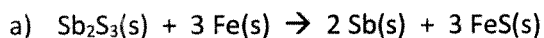


$$\Delta S^\circ = [(2)(28 \text{ J/mol}\cdot\text{K}) + (3)(189 \text{ J/mol}\cdot\text{K})] - [(1)(51 \text{ J/mol}\cdot\text{K}) + (3)(131 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = [623 \text{ J/mol}\cdot\text{K}] - [444 \text{ J/mol}\cdot\text{K}] = \boxed{179 \text{ J/mol}\cdot\text{K}}$$

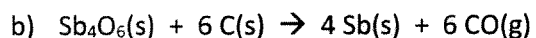
4. Calculating ΔS_{surr} from ΔH $\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$

Calculate ΔS_{surr} for each reaction at 25°C and 1 atm.



$$\Delta H = -125 \text{ kJ/mol}$$

$$\Delta S_{\text{surr}} = \frac{-(-125 \text{ kJ/mol})}{298 \text{ K}} = \boxed{0.419 \text{ kJ/mol}\cdot\text{K}}$$

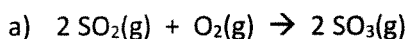


$$\Delta H = 778 \text{ kJ/mol}$$

$$\Delta S_{\text{surr}} = \frac{-(778 \text{ kJ/mol})}{298 \text{ K}} = \boxed{-2.61 \text{ kJ/mol}\cdot\text{K}}$$

5. Calculating ΔG from ΔH and ΔS $\Delta G = \Delta H - T\Delta S$

Calculate ΔG using the information provided for each reaction.

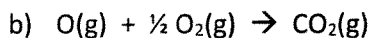


$$\Delta H^\circ = -198 \text{ kJ/mol}$$

$$\Delta S^\circ = -0.187 \text{ kJ/mol}\cdot\text{K}$$

$$\Delta S^\circ = -187 \text{ J/mol}\cdot\text{K}$$

$$\Delta G = -198 \text{ kJ/mol} - 298 \text{ K}(-0.187 \text{ kJ/mol}\cdot\text{K}) = \boxed{-142 \text{ kJ/mol}}$$



$$\Delta H^\circ = -283 \text{ kJ/mol}$$

$$\Delta S^\circ = -86.6 \text{ J/mol}\cdot\text{K}$$

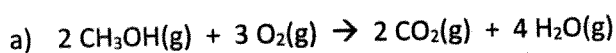
$$\Delta S^\circ = -0.0866 \text{ kJ/mol}\cdot\text{K}$$

$$\Delta G = -283 \text{ kJ/mol} - 298 \text{ K}(-0.0866 \text{ kJ/mol}\cdot\text{K})$$

$$\boxed{\Delta G = -257 \text{ kJ/mol}}$$

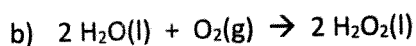
6. Calculating ΔG° from ΔG_f° $\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$

Calculate ΔG° using ΔG_f° data (Appendix 4) for each reaction.



$$\Delta G^\circ = [(2)(-394 \text{ kJ/mol}) + (4)(-229 \text{ kJ/mol})] - [(2)(-163 \text{ kJ/mol}) + (3)(0)]$$

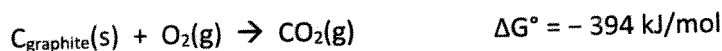
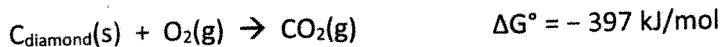
$$\Delta G^\circ = [-1704 \text{ kJ/mol}] - [-326 \text{ kJ/mol}] = \boxed{-1378 \text{ kJ/mol}}$$



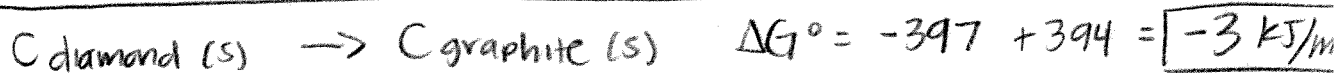
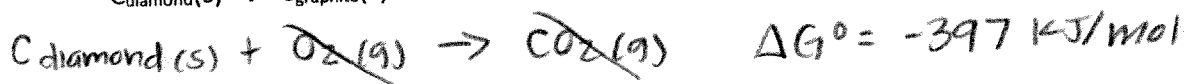
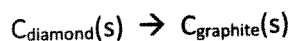
$$\Delta G^\circ = [(2)(-120.42 \text{ kJ/mol})] - [(2)(-237 \text{ kJ/mol}) + (1)(0)]$$

$$\Delta G^\circ = [-240.84 \text{ kJ/mol}] - [-474 \text{ kJ/mol}] = \boxed{233.16 \text{ kJ/mol}}$$

7. Calculating ΔG using Hess' Law



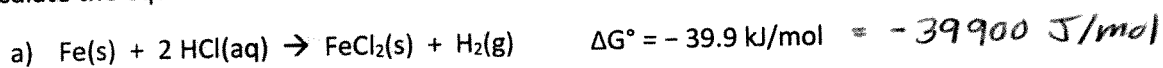
Using the information above, calculate ΔG° for the reaction below.



8. ΔG and K Calculations

$$\Delta G = -RT \ln K$$

Calculate the equilibrium constant for each reaction at 25°C.



$$\Delta G = -RT \ln K$$

$$-39.9 \times 10^3 \text{ J/mol} = -8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K}) \ln K$$

$$\ln K = 16.1 \quad \therefore K = e^{16.1} = \boxed{9.94 \times 10^6}$$



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

$$\Delta G = -1652 \text{ kJ/mol} - 298 \text{ K}(-0.543 \text{ kJ/mol} \cdot \text{K}) = -1490 \text{ kJ/mol}$$

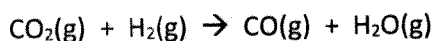
$$\Delta G = -RT \ln K$$

$$-1490 \times 10^3 \text{ J/mol} = -8.31 \text{ J/mol} \cdot \text{K} (298 \text{ K}) \ln K$$

$$\ln K = 602 \quad \therefore K = e^{602} \quad \boxed{K > 1}$$

9. Calculating T at Which Rxn Becomes Spontaneous/Nonspontaneous (ΔG changes sign)

Calculate the temperature at which the sign of ΔG changes from positive to negative. Assume that ΔH° and ΔS° are constant and do not change with temperature.



$$\Delta H^\circ = 41.2 \text{ kJ/mol}$$

$$\Delta S^\circ = 42.1 \text{ J/mol}\cdot\text{K}$$

$$\text{set } \Delta G = 0$$

$$\therefore T = \frac{\Delta H}{\Delta S}$$

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

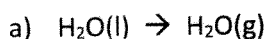
$$0 = \Delta H - T\Delta S$$

$$T\Delta S = \Delta H$$

$$T = \frac{41.2 \text{ kJ/mol}}{0.0421 \text{ kJ/mol}\cdot\text{K}} = \boxed{979 \text{ K}}$$

10. Phase Changes

Calculate the temperature at which the indicated phase change occurs.

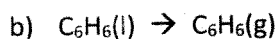


$$\Delta H_{\text{vap}} = 44 \text{ kJ/mol}$$

$$\Delta S_{\text{vap}} = 118.8 \text{ J/mol}\cdot\text{K}$$

$\Delta G = 0$ during phase change

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{44 \text{ kJ/mol}}{0.1188 \text{ kJ/mol}\cdot\text{K}} = \boxed{370 \text{ K}}$$



Substance	ΔH°_f (kJ/mol)	S° (J/mol \cdot K)
$\text{C}_6\text{H}_6(\text{l})$	48.99	173.3
$\text{C}_6\text{H}_6(\text{g})$	82.93	269.2

$$\Delta H_{\text{vap}} = 82.93 \text{ kJ/mol} - 48.99 \text{ kJ/mol} = 33.94 \text{ kJ/mol}$$

$$\Delta S_{\text{vap}} = 269.2 \text{ J/mol}\cdot\text{K} - 173.3 \text{ J/mol}\cdot\text{K} = 95.9 \text{ J/mol}\cdot\text{K}$$

$\Delta G = 0$ during phase change

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{33.94 \text{ kJ/mol}}{0.0959 \text{ kJ/mol}\cdot\text{K}} = \boxed{354 \text{ K}}$$