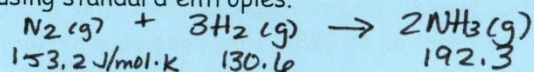


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Entropy and Gibb's Free Energy

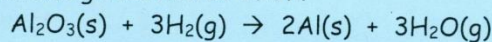
- Choose the sample of matter that has greater entropy in each pair.
 - 1 mol NaCl (s) or 1 mol of HCl(g) at 25°C.
 - 2 mol of HCl(g) or 1 mol of HCl(g) at 25°C.
 - 1 mol of HCl(g) or 1 mol of Ar(g) 25°C.
 - 1 mol of N₂(s) at 24 K or 1 mol of N₂(g) at 298K.
- Predict whether the entropy change (ΔS) of the system in each of the following reactions is positive or negative.
 - CaCO₃(s) \rightarrow CaO(s) + CO₂(g) **+**
 - N₂(g) + 3H₂(g) \rightarrow 2NH₃(g) **-**
 - HCl(g) + NH₃(g) \rightarrow NH₄Cl(s) **-**
 - 2SO₂(g) + O₂(g) \rightarrow 2SO₃(g) **-**

- Calculate $\Delta S^\circ_{\text{rxn}}$ for the synthesis of ammonia from N₂(g) and H₂(g) at 298K using standard entropies.



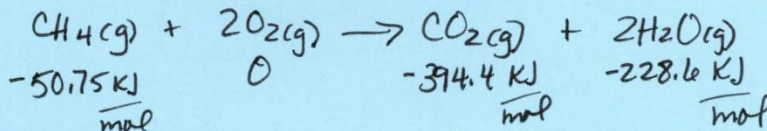
$$\Delta S = \left(2 \cdot \frac{192.3 \text{ J}}{\text{mol}\cdot\text{K}} \right) - \left[\left(1 \cdot \frac{153.2 \text{ J}}{\text{mol}\cdot\text{K}} \right) + \left(3 \cdot \frac{130.6 \text{ J}}{\text{mol}\cdot\text{K}} \right) \right] = \boxed{-198.3 \frac{\text{J}}{\text{K}}}$$

- Using standard entropies, calculate the standard entropy change, ΔS° , for the following reaction at 298K.



$$\Delta S = \left[\left(2 \cdot \frac{28.3 \text{ J}}{\text{mol}\cdot\text{K}} \right) + \left(3 \cdot \frac{188.7 \text{ J}}{\text{mol}\cdot\text{K}} \right) \right] - \left[\left(1 \cdot \frac{50.92 \text{ J}}{\text{mol}\cdot\text{K}} \right) + \left(3 \cdot \frac{130.6 \text{ J}}{\text{mol}\cdot\text{K}} \right) \right] = \boxed{+180.4 \frac{\text{J}}{\text{K}}}$$

- Calculate the standard free energy change, ΔG° , for the combustion of methane, CH₄, at 298K.



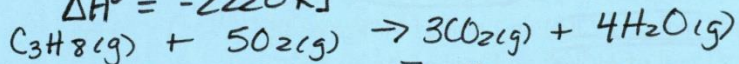
$$\Delta G^\circ = \left[\left(1 \cdot \frac{-394.4 \text{ kJ}}{\text{mol}} \right) + \left(2 \cdot \frac{-228.6 \text{ kJ}}{\text{mol}} \right) \right] - \left[\left(1 \cdot \frac{-50.75 \text{ kJ}}{\text{mol}} \right) + \left(2 \cdot 0 \right) \right]$$

$$\boxed{\Delta G^\circ = -800.9 \text{ kJ}}$$

6. For the combustion of propane, C_3H_8 , $\Delta H^\circ = -2220 \text{ kJ}$. Using S° values from the appendix of your book calculate ΔS for this reaction. Using $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ determine ΔG° for this reaction.

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

$$\Delta H^\circ = -2220 \text{ kJ}$$



$$\Delta S = \left[(3 \cdot 213.6 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + (4 \cdot 188.7 \frac{\text{J}}{\text{mol}\cdot\text{K}}) \right] - \left[(1 \cdot 270.2 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + (5 \cdot 205.0 \frac{\text{J}}{\text{mol}\cdot\text{K}}) \right]$$

$$\Delta S = 100.4 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 0.1004 \text{ kJ/mol}\cdot\text{K}$$

$$\Delta G = (-2220 \text{ kJ}) - (298.15 \text{ K} \cdot 0.1004 \frac{\text{kJ}}{\text{K}}) = \boxed{-2249 \text{ kJ}}$$

Using ΔG°_f from the appendix of your book, calculate the standard free energy change for the reaction at 298K. How does your prediction from above compare to this value?

$$\Delta G = \boxed{-2074.1 \text{ kJ}}$$

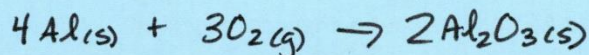
7. Phosgene, COCl_2 , was used as a war gas during World War I. It reacts with the moisture in the lungs to produce HCl , which causes the lungs to fill with fluid, leading to death of the victim. COCl_2 has a standard entropy, $S^\circ = 284 \text{ J/mol K}$ and $H^\circ = -223 \text{ kJ/mol}$. Calculate G° for $\text{COCl}_2(\text{g})$ in kJ/mol at body temperature, 37.0°C .

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

$$\Delta G = (-223 \text{ kJ}) - \left(310.15 \text{ K} \cdot \frac{284 \text{ J/K}}{1000 \text{ J/kJ}} \right)$$

$$\Delta G = -311 \text{ kJ}$$

8. Aluminum oxidizes rather easily, but forms a thin protective coating of Al_2O_3 that prevents further oxidation of the aluminum beneath. Use the data for H_f° and S° to calculate G° for $\text{Al}_2\text{O}_3(\text{s})$ in kJ/mol .



$$\Delta H = (2 \cdot -1676 \text{ kJ}) - (4 \cdot 0 + 3 \cdot 0) = -3352 \text{ kJ}$$

$$\Delta S = \left(2 \cdot \frac{50.92 \text{ J}}{1000 \text{ J/kJ}} \right) - \left[\left(4 \cdot \frac{28.3 \text{ J}}{1000 \text{ J/kJ}} \right) + \left(3 \cdot \frac{205.0 \text{ J}}{1000 \text{ J/kJ}} \right) \right] = -0.626 \text{ kJ}$$

$$\Delta G = (-3352 \text{ kJ}) - (298.15 \cdot (-0.626 \text{ kJ})) = -3538 \text{ kJ}$$

9. For the reaction $\text{Fe}_2\text{O}_3(\text{s}) + 3 \text{ CO}(\text{g}) \rightarrow 2 \text{ Fe}(\text{s}) + 3 \text{ CO}_2(\text{g})$

$\Delta G^\circ = -31.3 \text{ kJ}$. Calculate the standard free energy of formation of the ferric oxide, Fe_2O_3 , if ΔG°_f of $\text{CO} = -137 \text{ kJ/mol}$ and ΔG°_f of $\text{CO}_2 = -394 \text{ kJ/mol}$.

$$-740. \text{ kJ}$$

10. Predict the sign of $\Delta G^\circ_{\text{rxn}}$ for each of the following:

a. Melt ice

- (at high temp.)

b. Combustion of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$

- (all temp.)

c. Crystallization of a supersaturated solution of sodium acetate

- (low temp.)

d. The decomposition of water

- (high temp.)

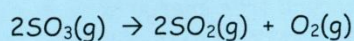
e. The formation of water from its elements.

- (low temp.)

11. What does ΔG tell us about a chemical reaction?

It indicates if a rxn is
spontaneous

12. Write two mathematical expressions that show how to calculate the standard Gibbs Free Energy change for the decomposition of sulfur trioxide from tabulated values:



$$\Delta G = \Delta H - T\Delta S \quad \text{or} \quad \Delta G^\circ = \sum \nu_p \Delta G^\circ_{\text{f}(\text{products})} - \sum \nu_r \Delta G^\circ_{\text{f}(\text{reactants})}$$

For this reaction $\Delta H^\circ_{\text{rxn}} = 197.78 \text{ kJ/mol}$ and $\Delta S^\circ_{\text{rxn}} = 188.06 \text{ J/mol K}$.
Calculate $\Delta G^\circ_{\text{rxn}}$ at 298K.

$$\Delta G^\circ_{\text{rxn}} = 141.74 \text{ kJ/mol}$$