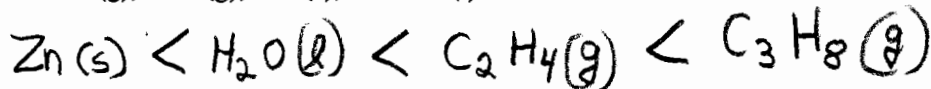


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$R = 8.314 \text{ J}/(\text{mol}\cdot\text{K})$    
 $\Delta S^\circ = \sum nS^\circ_{(\text{products})} - \sum nS^\circ_{(\text{reactants})}$    
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 $\Delta G^\circ = \sum nG^\circ_{(\text{products})} - \sum nG^\circ_{(\text{reactants})}$   
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$    
 $\Delta G = \Delta G^\circ + RT \ln Q$    
 $\Delta G^\circ = -RT \ln K$

1. Arrange these compounds in order of increasing standard molar entropy at 25°C:  
 $\text{C}_3\text{H}_8(\text{g})$ ,  $\text{C}_2\text{H}_4(\text{g})$ ,  $\text{ZnS}(\text{s})$ , and  $\text{H}_2\text{O}(\text{l})$ .



2. Which one of the following reactions would you expect to have highest  $\Delta S^\circ$ ?

- A)  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$   
 B)  $\text{C}_2\text{H}_2(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$   
 C)  $\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$   
 D)  $\text{C}_2\text{H}_6(\text{g}) + \frac{7}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$

Largest change in moles of gas.

3. Calculate  $\Delta S^\circ$  at 25°C for the reduction of  $\text{PbO}(\text{s})$ ,  $2\text{PbO}(\text{s}) + \text{C}(\text{s}) \rightarrow 2\text{Pb}(\text{s}) + \text{CO}_2(\text{g})$  given these absolute entropies:

|                         | $S^\circ$ (J/K·mol) |
|-------------------------|---------------------|
| $\text{PbO}(\text{s})$  | 69.45               |
| $\text{C}(\text{s})$    | 5.7                 |
| $\text{Pb}(\text{s})$   | 64.89               |
| $\text{CO}_2(\text{g})$ | 213.6               |

$$\Delta S^\circ = \sum n\Delta S^\circ_{\text{products}} - \sum n\Delta S^\circ_{\text{reactants}}$$

$$= [2(64.89) + 213.6] - [2(69.45) + 5.7]$$

$$= 198.7 \text{ J/K}\cdot\text{mol}$$

4. HI has a normal boiling point of  $-35.4^\circ\text{C}$ , and its  $\Delta H_{\text{vap}}$  is 21.16 kJ/mol. Calculate the molar entropy of vaporization ( $\Delta S_{\text{vap}}$ ).

$$\Delta S_{\text{vap}} = \frac{\Delta H}{T} = \frac{21.16 \times 10^3 \text{ J/mol}}{(-35.4 + 273) \text{ K}} = 89.1 \text{ J/K}\cdot\text{mole}$$

$$\approx 0.0891 \text{ kJ/K}\cdot\text{mole}$$

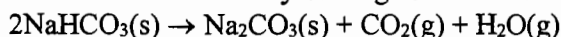
5. Calculate  $\Delta G^\circ$  for the reaction  $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HNO}_3(\text{l}) + \text{NO}(\text{g})$ .

|                                | $\Delta G^\circ_f$ (kJ/mol) |
|--------------------------------|-----------------------------|
| $\text{H}_2\text{O}(\text{l})$ | -237.2                      |
| $\text{HNO}_3(\text{l})$       | -79.9                       |
| $\text{NO}(\text{g})$          | 86.7                        |
| $\text{NO}_2(\text{g})$        | 51.8                        |

$$\Delta G^\circ = [2(-79.9) + 86.7] - [3(51.8) + (-237.2)]$$

$$\Delta G^\circ = 8.7 \text{ kJ/mole}$$

6. Sodium carbonate can be made by heating sodium bicarbonate:



Given that  $\Delta H^\circ = 128.9 \text{ kJ/mol}$  and  $\Delta G^\circ = 33.1 \text{ kJ/mol}$  at 25°C, above what minimum temperature will the reaction become spontaneous?

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

$$33.1 \text{ kJ/mol} = 128.9 \text{ kJ/mol} - 298(\text{K}) \Delta S$$

$$\Delta S = 0.321 \text{ kJ/K}\cdot\text{mol}$$

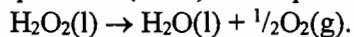
Then: @ Eq  $0 = 128.9 \text{ kJ/mol} - T(0.321 \text{ kJ/K}\cdot\text{mol})$

$$T = 400 \text{ K}$$

$$\text{So @ } T > 400 \text{ K}$$

—over—

7. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) decomposes according to the equation



Calculate  $K_p$  for this reaction at  $25^\circ\text{C}$ . ( $\Delta H^\circ = -98.2 \text{ kJ/mol}$ ,  $\Delta S^\circ = 70.1 \text{ J/K}\cdot\text{mol}$ )

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -98.2 \frac{\text{kJ}}{\text{mol}} - (298\text{K} \cdot 0.0701 \frac{\text{kJ}}{\text{mol}\cdot\text{K}}) \\ &= -119.1 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

$$\begin{aligned} \text{Next: } \Delta G^\circ &= -RT \ln K_p \\ -119.1 \times 10^3 \text{ J/mol} &= \ln K_p \\ (-8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \cdot 298\text{K}) &= \ln K_p \\ 48.067 &= \ln K_p \quad K_p = 7.5 \times 10^{20} \end{aligned}$$

8. At  $1500^\circ\text{C}$  the equilibrium constant for the reaction  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$  has the value  $K_p = 1.4 \times 10^{-7}$ . Calculate  $\Delta G^\circ$  for this reaction at  $1500^\circ\text{C}$ .

$$\begin{aligned} \Delta G^\circ &= -RT \ln K \\ &= -8.314(1773) \ln 1.4 \times 10^{-7} = 232632 \text{ J/mol} \\ &= 233 \text{ kJ/mol} \end{aligned}$$

9. Assuming  $\Delta S^\circ$  and  $\Delta H^\circ$  do not vary with temperature, at what temperature will the reaction shown below become spontaneous?



$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ 0 &= 131.3 \text{ kJ/mol} - T(0.1336 \text{ kJ/K}\cdot\text{mol}) \\ T &= 982.8 \text{ K} \\ &\text{above } 710^\circ\text{C} \end{aligned}$$

10. For the reaction  $\text{H}_2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ ,  $\Delta H^\circ = -106 \text{ kJ/mol}$  and  $\Delta S^\circ = 58 \text{ J/K}\cdot\text{mol}$  at  $25^\circ\text{C}$ . Calculate  $\Delta G^\circ$  for this reaction at this temperature.

$$\begin{aligned} \Delta G &= -106 \text{ kJ/mol} - 298\text{K}(0.058 \text{ J/K}\cdot\text{mol}) \\ \Delta G &= -123 \text{ kJ/mol} \end{aligned}$$