

18-35. Calculate ΔS° for the vaporization of ethanol at the boiling point of 78.3 °C. $\Delta H^\circ_{\text{vap}} = 39.3 \text{ kJ/mol}$

Step 1: decide which relationship to use

$$\Delta S = q_{\text{rev}}/T$$

Step 2: determine q_{rev}

q_{rev} is heat exchanged between system and surroundings— $\Delta H^\circ_{\text{vap}}$ is heat absorbed by system from surroundings to get ethanol to boil

$$\therefore q_{\text{rev}} = \Delta H^\circ_{\text{vap}} = 39.3 \text{ kJ/mol}$$

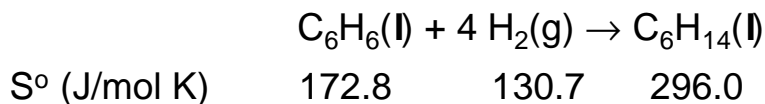
Step 3: calculate ΔS° for process

$$\Delta S^\circ = (39,300 \text{ J/mol})/(351.5 \text{ K}) = 112 \text{ J/mol K}$$

18-47. Calculate $\Delta S^\circ_{\text{sys}}$ at 25 °C for the reaction
 $\text{C}_6\text{H}_6(\text{l}) + 4 \text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{14}(\text{l})$

Is the reaction reactant- or product-favored?

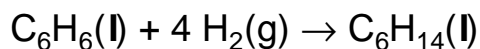
Step 1: look up S° 's for all species



Step 2: calculate $\Delta S^\circ_{\text{rxn}}$ using Hess' Law

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 296.0 - \{172.8 + 4(130.7)\} \\ &= -399.6 \text{ J/mol K}\end{aligned}$$

18-47 (con't). Calculate $\Delta S_{\text{sys}}^{\circ}$ at 25 °C for the reaction



Is the reaction reactant- or product-favored?

Step 3: Is the reaction reactant- or product-favored?

Need $\Delta H_{\text{rxn}}^{\circ}$ to answer question ($\Delta G = \Delta H - T\Delta S$):

Since the term $-T\Delta S_{\text{rxn}}^{\circ}$ will always be positive,

if $\Delta H_{\text{rxn}}^{\circ}$ is positive, the reaction will always be reactant-favored;

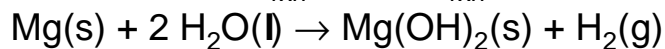
if $\Delta H_{\text{rxn}}^{\circ}$ is negative, the reaction will be product-favored at low T, and reactant-favored at high T

18-57. The reaction $\text{Mg}(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{Mg}(\text{OH})_2(\text{s}) + \text{H}_2(\text{g})$ can be used to heat food. Determine whether the reaction is product-favored at 25 °C.

a. Calculate $\Delta S_{\text{universe}}$.

b. Verify results by calculating $\Delta G_{\text{rxn}}^{\circ}$.

Step 1: Calculate $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$



$$\Delta H_{\text{f}}^{\circ} \quad 0.0 \quad -285.8 \quad -924.5 \quad 0.0$$

$$S^{\circ} \quad 32.7 \quad 69.9 \quad 63.2 \quad 130.7$$

$$\Delta H_{\text{rxn}}^{\circ} = -924.5 - 2(-285.8) = -352.9 \text{ kJ}$$

$$\Delta S_{\text{rxn}}^{\circ} = \{63.2 + 130.7\} - \{32.7 + 2(69.9)\} = 21.4 \text{ J/K}$$

18-57 (con't.). The reaction $\text{Mg(s)} + 2 \text{H}_2\text{O(l)} \rightarrow \text{Mg(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$ can be used to heat food. Determine whether the reaction is product-favored at 25 °C.

- Calculate $\Delta S_{\text{universe}}$.
- Verify results by calculating $\Delta G^{\circ}_{\text{rxn}}$.

Step 2: Calculate $\Delta S^{\circ}_{\text{surr}}$

$$\Delta S^{\circ}_{\text{surr}} = q_{\text{rev}}/T_{\text{surr}}$$

$$q_{\text{rev}} = -\Delta H^{\circ}_{\text{rxn}} = -(-352.9 \text{ kJ})$$

$$\Delta S^{\circ}_{\text{surr}} = 352,900 \text{ J}/298 \text{ K} = 1184 \text{ J/K}$$

Step 3: Calculate $\Delta S^{\circ}_{\text{univ}}$

$$\Delta S^{\circ}_{\text{univ}} = \Delta S^{\circ}_{\text{rxn}} + \Delta S^{\circ}_{\text{surr}}$$

$$= 21.4 \text{ J/K} + 1184 \text{ J/K} = 1205 \text{ J/K}$$

18-57 (con't.). The reaction $\text{Mg(s)} + 2 \text{H}_2\text{O(l)} \rightarrow \text{Mg(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$ can be used to heat food. Determine whether the reaction is product-favored at 25 °C.

- Calculate $\Delta S_{\text{universe}}$.
- Verify results by calculating $\Delta G^{\circ}_{\text{rxn}}$.

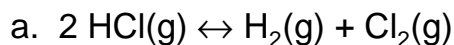
Step 4: is reaction product-favored?

$$\Delta G^{\circ}_{\text{rxn}} = \Delta H^{\circ}_{\text{rxn}} - T\Delta S^{\circ}_{\text{rxn}}$$

$$= -352,900 \text{ J} - (298 \text{ K})(21.4 \text{ J/K})$$

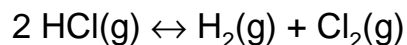
$$= -359.3 \text{ kJ}$$

18-74. Calculate K_{eq} for the following reactions at 298.15 K



Remember: $\Delta G^\circ_{rxn} = -RT \ln(K_{eq})$

Step 1: calculate ΔG°_{rxn}



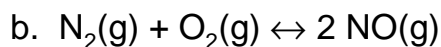
$$\Delta G^\circ_f(\text{kJ/mol}) \quad -95.30 \quad 0.00 \quad 0.00$$

$$\Delta G^\circ_{rxn} = \{0.00 + 0.00\} - 2(-95.30) = 190.6 \text{ kJ/mol}$$

Step 2: calculate K_p

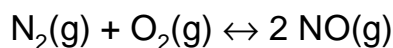
$$K_p = \exp\left\{\frac{-\Delta G^\circ_{rxn}}{RT}\right\} = \exp\left\{\frac{-190,600 \text{ kJ/mol}}{(8.314 \text{ J/molK})(298.15 \text{ K})}\right\}$$
$$= 4.04 \times 10^{-34}$$

18-74. Calculate K_{eq} for the following reactions at 298.15 K



Remember: $\Delta G^\circ_{rxn} = -RT \ln(K_{eq})$

Step 1: calculate ΔG°_{rxn}



$$\Delta G^\circ_f(\text{kJ/mol}) \quad 0.00 \quad 0.00 \quad 51.3$$

$$\Delta G^\circ_{rxn} = 2(51.3) - \{0.00 + 0.00\} = 102.6 \text{ kJ/mol}$$

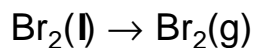
Step 2: calculate K_p

$$K_p = \exp\left\{\frac{-\Delta G^\circ_{rxn}}{RT}\right\} = \exp\left\{\frac{-102,600 \text{ kJ/mol}}{(8.314 \text{ J/molK})(298.15 \text{ K})}\right\}$$
$$= 1.06 \times 10^{-18}$$

18-124. Estimate the following from the data in Appendix J:

a. Boiling point of Br₂

Step 1: calculate $\Delta S^\circ_{\text{rxn}}$ and $\Delta H^\circ_{\text{rxn}}$



$$S^\circ(\text{J/mol K}) \quad 152.231 \quad 245.463$$

$$\Delta H^\circ_f(\text{kJ/mol}) \quad 0.000 \quad 30.907$$

$$\Delta S^\circ_{\text{rxn}} = 245.463 - 152.231 = 93.232 \text{ J/mol K}$$

$$\Delta H^\circ_{\text{rxn}} = 30.907 - 0.000 = 30.907 \text{ kJ/mol}$$

18-124. Estimate the following from the data in Appendix J:

a. Boiling point of Br₂

Step 2: Calculate T_{vap}

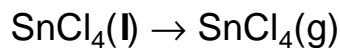
$$\Delta S^\circ_{\text{rxn}} = q_{\text{rev}}/T = \Delta H^\circ_{\text{rxn}}/T \text{ at equilibrium (such as a phase change)}$$

$$\begin{aligned} \therefore T_{\text{vap}} &= \Delta H^\circ_{\text{rxn}}/\Delta S^\circ_{\text{rxn}} \\ &= (30907 \text{ J/mol})/(93.232 \text{ J/mol K}) \\ &= 331.5 \text{ K (literature value = 332.0 K)} \end{aligned}$$

18-124. Estimate the following from the data in Appendix J:

b. Boiling point of SnCl_4

Step 1: calculate $\Delta S^\circ_{\text{rxn}}$ and $\Delta H^\circ_{\text{rxn}}$



$$S^\circ(\text{J/mol K}) \quad 258.6 \quad 365.8$$

$$\Delta H^\circ_f(\text{kJ/mol}) \quad -511.3 \quad -471.5$$

$$\Delta S^\circ_{\text{rxn}} = 365.8 - 258.6 = 107.2 \text{ J/mol K}$$

$$\Delta H^\circ_{\text{rxn}} = -471.5 - (-511.3) = 39.8 \text{ kJ/mol}$$

18-124. Estimate the following from the data in Appendix J:

a. Boiling point of SnCl_4

Step 2: Calculate T_{vap}

$\Delta S^\circ_{\text{rxn}} = q_{\text{rev}}/T = \Delta H^\circ_{\text{rxn}}/T$ at equilibrium (such as a phase change)

$$\begin{aligned} \therefore T_{\text{vap}} &= \Delta H^\circ_{\text{rxn}} / \Delta S^\circ_{\text{rxn}} \\ &= (39800 \text{ J/mol}) / (107.2 \text{ J/mol K}) \\ &= 371.3 \text{ K} \quad (\text{literature value} = 387.3 \text{ K}) \end{aligned}$$