

Standard molar entropy (continued)

- S° can be affected by changing the thermal and positional disorder in different ways

➤ Dissolution of solids or liquids

- Usually S° increases as solids or liquids dissolve
 - Mixing increases the positional disorder, so $S^\circ \uparrow$

Dissolving liquids & solids $\Rightarrow S^\circ \uparrow$

- Sometimes S° decreases as substances dissolve, especially for ionic solids with small highly charged ions (Al^{3+} , Mg^{2+} ...)

- Extensive ion hydration decreases the positional disorder of the water molecules which overcomes the increase in the disorder due to mixing, so $S^\circ \downarrow$

Hydration $\Rightarrow S^\circ \downarrow$

➤ Dissolution of gases

- S° decreases as gases dissolve in liquids or solids
 - The molecules of the gas are more restricted in solution, so $S^\circ \downarrow$

Dissolving gases $\Rightarrow S^\circ \downarrow$

- S° increases as gases are mixed with each other
 - Mixing increases the positional disorder, so $S^\circ \uparrow$

Mixing of gases $\Rightarrow S^\circ \uparrow$

➤ Atomic size or molecular complexity

- For elements and for similar compounds in the same phase, S° increases with the molar mass (the # of electrons \uparrow , so $S^\circ \uparrow$)

Molar mass $\uparrow \Rightarrow S^\circ \uparrow$

- For compounds in the same phase, S° increases with the chemical complexity ($S^\circ \uparrow$ with the number of atoms in the compound)

atoms $\uparrow \Rightarrow S^\circ \uparrow$

- For organic compounds in the same phase, S° increases with the length of the hydrocarbon chain

Length of chain $\uparrow \Rightarrow S^\circ \uparrow$

- The effect of the physical state on S° usually dominates the effect of molecular complexity

Examples: Which of the following has higher S°

a) Air at 25°C or air at 35°C

- S° increases with T

b) $\text{CH}_3\text{OH}(\text{l})$ at 25°C or $\text{CH}_3\text{OH}(\text{g})$ at 25°C

- S° increases from liquid to gas

c) $\text{NaCl}(\text{s})$ at 25°C or $\text{NaCl}(\text{aq})$ at 25°C

- S° typically increases with dissolution of solids

d) $\text{N}_2(\text{g})$ at 25°C or $\text{N}_2(\text{aq})$ at 25°C

- S° decreases with dissolution of gases

e) $\text{HCl}(\text{g})$ at 25°C or $\text{HBr}(\text{g})$ at 25°C

- S° increases with increasing the molar mass

f) $\text{CO}_2(\text{g})$ at 25°C or $\text{CH}_3\text{OH}(\text{g})$ at 25°C

- S° increases with increasing the molecular complexity (# atoms)

20.2 Calculating the Entropy Change of a Reaction

Entropy Changes in the System

- **Standard entropy of reaction (ΔS_r°)** – the difference between the standard entropies of the products and the reactants

$$\Delta S_r^\circ = \sum m S^\circ(\text{products}) - \sum n S^\circ(\text{reactants})$$

(n, m - stoichiometric coefficients of reactants or products)

→ The equation is similar to the Hess's law expression for the standard reaction enthalpy

$$\Delta H_r^\circ = \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$$

Example: Calculate the standard entropy (ΔS_r°) of the reaction $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

$$\Delta S_r^\circ = \sum m S^\circ(\text{products}) - \sum n S^\circ(\text{reactants})$$

$$\Delta S_r^\circ = 2 \times S^\circ(\text{NO}_2(\text{g})) - 1 \times S^\circ(\text{N}_2\text{O}_4(\text{g}))$$

→ From **Appendix B**:

$$\Delta S_r^\circ = 2 \text{ mol} \times 239.9 \text{ J/mol}\cdot\text{K} - 1 \text{ mol} \times 304.3 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_r^\circ = \boxed{175.5 \text{ J/K}}$$

➤ For reactions involving gases:

➤ $\Delta S_r^\circ > 0$ if (# mol gaseous products) > (# mol gaseous reactants)

➤ $\Delta S_r^\circ < 0$ if (# mol gaseous products) < (# mol gaseous reactants)

Entropy Changes in the Surroundings

- The surroundings function as a heat sink for the system (reaction) → $q_{\text{surr}} = -q_{\text{sys}}$
 - **Exothermic** reactions – heat is lost by the system and gained by the surroundings which increases the thermal disorder in the surroundings
 - $q_{\text{sys}} < 0 \Rightarrow q_{\text{surr}} > 0$ and $\Delta S_{\text{surr}} > 0$
 - **Endothermic** reactions – heat is gained by the system and lost by the surroundings which reduces the thermal disorder in the surroundings
 - $q_{\text{sys}} > 0 \Rightarrow q_{\text{surr}} < 0$ and $\Delta S_{\text{surr}} < 0$
- ΔS_{surr} is proportional to the amount of heat transferred → $\Delta S_{\text{surr}} \propto q_{\text{surr}} \Rightarrow \Delta S_{\text{surr}} \propto -q_{\text{sys}}$

➤ ΔS_{surr} is inversely proportional to the T since the heat transfer changes the disorder of the surroundings more at lower $T \Rightarrow \Delta S_{\text{surr}} \propto 1/T$

$$\Rightarrow \Delta S_{\text{surr}} = -q_{\text{sys}}/T$$

➤ At constant pressure ($q_p = \Delta H$)

$$\Rightarrow \Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$$

→ The equation allows the calculation of ΔS_{surr} from the reaction enthalpy and the temperature (applies strictly only at constant T and P)

➤ According to the **2nd law**, for a spontaneous reaction

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

➤ Substituting ΔS_{surr} with $-\Delta H_{sys}/T$ leads to

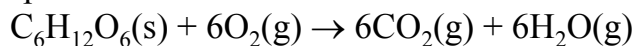
$$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0$$

→ The equation allows the calculation of ΔS_{univ} from the reaction entropy and enthalpy and the temperature (applies strictly at constant T and P)

→ The equation provides a **criterion for spontaneity** in any systems at constant T and P

- **Positive ΔS_{univ}** (spontaneous process) is favored by
 - **Positive entropy of reaction** ($\Delta S_{sys} > 0$) – the disorder of the system increases
 - **Negative enthalpy of reaction** ($\Delta H_{sys} < 0$) – the disorder of the surroundings increases

Example: Is the combustion of glucose spontaneous at 25°C?



→ Calculate ΔS_{sys}^o and ΔH_{sys}^o using Appendix B

$$\Delta S_r^o = [6 \times S^o(CO_2(g)) + 6 \times S^o(H_2O(g))] - [1 \times S^o(C_6H_{12}O_6(s)) + 6 \times S^o(O_2(g))]$$

$$\Delta S_r^o = [6(214) + 6(189)] - [1(212) + 6(205)] = \mathbf{976 \text{ J/K}}$$

$$\Delta H_r^o = [6 \times \Delta H_f^o(CO_2(g)) + 6 \times \Delta H_f^o(H_2O(g))] - [1 \times \Delta H_f^o(C_6H_{12}O_6(s)) + 6 \times \Delta H_f^o(O_2(g))]$$

$$\Delta H_r^o = [6(-394) + 6(-242)] - [1(-1273)] = \mathbf{-2543 \text{ kJ}}$$

$$\Delta S_{sys}^o = \mathbf{0.976 \text{ kJ/K}}$$

$$\Delta S_{surr}^o = -\Delta H_{sys}^o/T = -(-2543 \text{ kJ})/(298 \text{ K}) = \mathbf{8.53 \text{ kJ/K}}$$

$$\Delta S_{univ}^o = 0.976 + 8.53 = \mathbf{9.51 \text{ kJ/K} > 0} \rightarrow \mathbf{\text{spontaneous}}$$

Entropy Changes and the Equilibrium State

- $\Delta S_{univ} > 0$ → the forward reaction is spontaneous
 - $\Delta S_{univ} < 0$ → the forward reaction is non-spontaneous (the reverse reaction is spontaneous)
 - $\Delta S_{univ} = 0$ → the reaction is at equilibrium
 - ⇒ At equilibrium: $\Delta S_{univ}^o = \Delta S_{sys}^o - \Delta H_{sys}^o/T = 0$
 - ⇒ At equilibrium: $\Delta S_{sys}^o = \Delta H_{sys}^o/T$
- The equation is useful for calculating the entropies of phase changes during which the system is at equilibrium at constant T and P

Example: Calculate ΔS_{vap}^o of H₂O at its normal b.p.

$$\rightarrow \Delta H_{vap}^o = 40.7 \text{ kJ per 1 mol of H}_2\text{O}$$

$$\rightarrow \Delta S_{vap}^o = \Delta H_{vap}^o/T = 40.7 \text{ kJ} / 373 \text{ K} = \mathbf{0.109 \text{ kJ/K}}$$

Spontaneous Exo and Endothermic Reactions

$$\Delta S_{univ}^o = \Delta S_{sys}^o + \Delta S_{surr}^o > 0$$

➤ For **exothermic** reactions $\Delta S_{surr} = -\Delta H_{sys}/T > 0$

➤ If $\Delta S_{sys} > 0$, the reaction is spontaneous

➤ If $\Delta S_{sys} < 0$, the reaction is spontaneous only if the increase of S_{surr} is greater than the decrease of S_{sys}

➤ For **endothermic** reactions $\Delta S_{surr} = -\Delta H_{sys}/T < 0$

➤ If $\Delta S_{sys} > 0$, the reaction is spontaneous only if the increase of S_{sys} is greater than the decrease of S_{surr}

➤ If $\Delta S_{sys} < 0$, the reaction is not spontaneous

Example: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + \text{heat}$

Exothermic $\Rightarrow \Delta S_{surr} > 0$

Less gaseous products $\Rightarrow \Delta S_{sys} < 0$ | ΔS_{surr} dominates \rightarrow **spontaneous**