

Thermodynamics: The Direction of Chemical Reactions

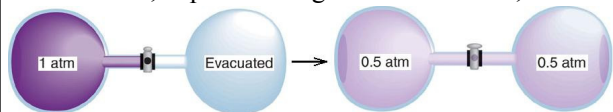
– Thermodynamics has two major aspects:

- Conservation of energy (1st law)
- Direction of processes (2nd law)

20.1 The 2nd Law of Thermodynamics

- **Spontaneous changes** – occur without any external influence

Examples: Aging, rusting, heat transfer from hot to cold, expansion of gases into vacuum, etc.

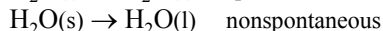
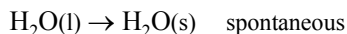


- **Nonspontaneous changes** – require an external force or energy in order to occur

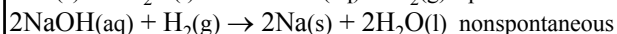
Examples: Refrigeration (heat transfer from cold to hot), evacuation of flasks by vacuum pumps, etc.

- If a process is spontaneous in one direction, it is not spontaneous in the other

Example: At -20°C, water freezes spontaneously, but ice does not melt spontaneously:



Example: At 25°C:



Limitations of the 1st Law

- The 1st law states that the **total energy of the universe is constant** ($E_{\text{univ}} = \text{const.}$)

→ E_{univ} can be separated into two parts, energy of the system, E_{sys} , and energy of its surroundings, E_{surr}

$$\Rightarrow E_{\text{univ}} = E_{\text{sys}} + E_{\text{surr}} \quad \Rightarrow \Delta E_{\text{univ}} = \Delta E_{\text{sys}} + \Delta E_{\text{surr}}$$

→ Since $E_{\text{univ}} = \text{const.}$, $\Delta E_{\text{univ}} = 0$

$$\Rightarrow \Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0 \quad \Rightarrow \Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$$

→ Since $\Delta E = q + w$ $\Rightarrow (q + w)_{\text{sys}} = -(q + w)_{\text{surr}}$

→ Energy (heat and/or work) released by the system is absorbed by its surroundings and vice versa

→ The 1st law doesn't explain the direction of spontaneous processes since energy conservation can be achieved in either direction

The Sign of ΔH and Spontaneity

- The sign of ΔH has been used (especially by organic chemists) to predict spontaneous changes – **not a reliable indicator**

➤ In most cases spontaneous reactions are **exothermic** ($\Delta H < 0$) → combustion, formation of salts from elements, neutralization, rusting, ...

➤ In some cases, spontaneous reactions can be **endothermic** ($\Delta H > 0$) → dissolution of many salts, melting and vaporization at high T , ...

→ A common feature of all **spontaneous endothermic reactions** is that their products are less ordered than the reactants (**disorder** ↑ during the reaction)

Example: Solid → Liquid → Gas

most ordered

least ordered

The Meaning of Disorder and Entropy

- **Macro-state** – the macroscopic state of a system described by its parameters (P , V , n , T , E , H , etc.)

➤ Spontaneous processes proceed from macro-states that are less probable toward ones that are more probable

- **Micro-state** – one of the possible microscopic ways through which the macro-state can be achieved

➤ Refers to one of the possible ways the total energy can be distributed over the quantized energy levels of the system

➤ This includes energy levels related to all possible motions of the molecules (translational, rotational, vibrational, etc.)

- More probable macro-states are those that can be achieved in a larger number of different ways (micro-states), and therefore, are more disordered

- In thermodynamics, the disorder of a macro-state is measured by the **statistical probability**, W → the number of different ways the energy can be distributed over the quantized energy levels of the system while still having the same total energy, or simply the number of micro-states through which the macro-state can be achieved

Example: Arrangement of 2 particles (x and o) in 3 possible positions →

x	o		o	x	
	x	o		o	x
o		x	x		o

→ There are 6 possible arrangements ($W = 6$)

→ Increasing the # of possible positions increases W

$$\uparrow W \Leftrightarrow \uparrow \text{Disorder}$$

- **Entropy (S)** – a state function related to the disorder of the system

– Boltzmann equation $\rightarrow S = k \ln(W)$

$\rightarrow k = 1.38 \times 10^{-23} \text{ J/K}$ (Boltzmann constant)

$$\uparrow W \Leftrightarrow \uparrow \text{Disorder} \Leftrightarrow \uparrow S$$

- S is a state function – depends only on the present state of the system and not on the way it arrived in that state

\Rightarrow The entropy change, $\Delta S = S_{\text{final}} - S_{\text{initial}}$, is path independent

\Rightarrow If $\Delta S > 0$, the entropy and the disorder increase

\Rightarrow If $\Delta S < 0$, the entropy and the disorder decrease

- The entropy and the disorder of a system can be increased in two basic ways:

– Heating (increases the **thermal disorder**)

– Expansion, mixing or phase changes (increase the **positional disorder**)

Note: Both thermal and positional disorder have the same origin (the number of possible micro-states)

Example: Gases expand spontaneously in vacuum.

\rightarrow During the expansion the total energy does not change (no heat is exchanged and no work is done since $P_{\text{ext}} = 0$)

\rightarrow The volume increases so the number of possible positions available to the particles increases $\Rightarrow W \uparrow$

\Rightarrow The process is driven by increase in the positional disorder and thus increase in the entropy

Entropy and the 2nd Law

- \Rightarrow The entropy of the system alone can not be used as a criterion for spontaneity

\Rightarrow Spontaneous processes can have $\Delta S > 0$ or $\Delta S < 0$

- \Rightarrow The true criterion for spontaneity is the entropy of the universe (S_{univ})

- **The 2nd law of thermodynamics** – for any spontaneous process, the entropy of the universe increases ($\Delta S_{\text{univ}} > 0$)

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

- There are no restrictions on the signs of ΔS_{sys} and ΔS_{surr} as long as the sum of the two is greater than zero

Standard Molar Entropies and the 3rd Law

- **The 3rd law of thermodynamics** – the entropy of a perfect crystal at the absolute zero is zero (As $T \rightarrow 0\text{K}$, $S_{\text{sys}} \rightarrow 0$)

– At the absolute zero, the particles of the crystal achieve the lowest possible energy and there is only one way they can be arranged ($W = 1$)

$$\Rightarrow S_{\text{sys}} = k \ln(1) = k (0) = 0$$

– The 3rd law allows the use of **absolute entropies**

\Rightarrow The entropy of a substance at a given T is equal to the entropy increase accompanying the heating of the substance from 0 K that T

- **Standard molar entropy (S°)** – the entropy of 1 mol of a substance in its standard state and a specified temperature (usually 298 K)

– **Standard state** – 1 atm for gases, 1 M for solutions, pure for liquids and solids

– Units of $S^\circ \rightarrow \text{J/mol}\cdot\text{K}$

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

\Rightarrow **Temperature changes** – for a given substance, S° increases as the temperature is increased

$$\uparrow T \Rightarrow \uparrow S^\circ$$

\rightarrow As $T \uparrow$, the average E_k of the molecules \uparrow and the # of ways to distribute E_k among the particles \uparrow so W and $S^\circ \uparrow$

\Rightarrow **Phase changes** – for a given substance, S° increases as the substance is converted from solid to liquid to gas

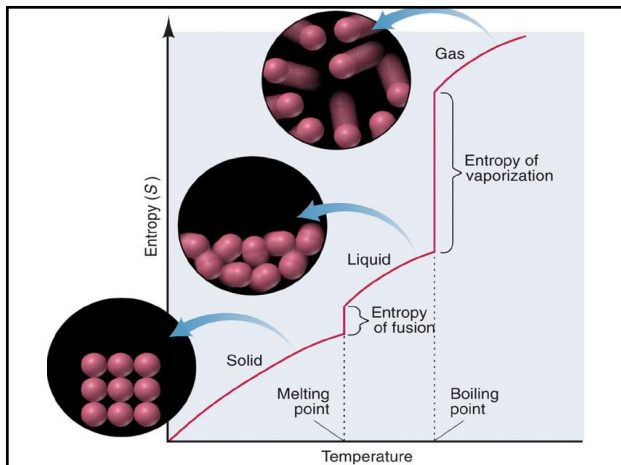
$$S^\circ_{\text{(solid)}} < S^\circ_{\text{(liquid)}} < S^\circ_{\text{(gas)}}$$

\rightarrow In the liquid and especially in the gas phase, the particles have more freedom to move around and thus higher positional disorder

\Rightarrow Within each phase, the entropy increases gradually with increasing T

\Rightarrow Since phase changes occur at constant T , a sharp change in entropy is observed as the T passes through the melting or boiling points

\Rightarrow Since the gas phase has much higher S° than the liquid and solid phases, $\Delta S^\circ_{\text{vap}} \gg \Delta S^\circ_{\text{fus}}$



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

$$\rightarrow q_{\text{sys}} < 0 \Rightarrow q_{\text{surr}} > 0 \text{ and } \boxed{\Delta S_{\text{surr}} > 0}$$

➤ **Endothermic** reactions – heat is gained by the system and lost by the surroundings which reduces the thermal disorder in the surroundings

$$\rightarrow q_{\text{sys}} > 0 \Rightarrow q_{\text{surr}} < 0 \text{ and } \boxed{\Delta S_{\text{surr}} < 0}$$

➤ 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 ($q_p = \Delta H$)

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

→ 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 $-\Delta H_{\text{sys}}/T$ leads to

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

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

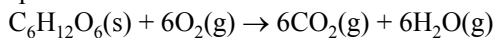
→ The equation provides a **criterion for spontaneity** in any systems at constant T and P

➤ **Positive ΔS_{univ}** (spontaneous process) is favored by

➤ **Positive entropy of reaction** ($\Delta S_{\text{sys}} > 0$) – the disorder of the system increases

➤ **Negative enthalpy of reaction** ($\Delta H_{\text{sys}} < 0$) – the disorder of the surroundings increases

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



→ Calculate $\Delta S_{\text{sys}}^\circ$ and $\Delta H_{\text{sys}}^\circ$ using Appendix B

$$\Delta S_r^\circ = [6 \times S^\circ(\text{CO}_2(\text{g})) + 6 \times S^\circ(\text{H}_2\text{O}(\text{g}))] - [1 \times S^\circ(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6 \times S^\circ(\text{O}_2(\text{g}))]$$

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

$$\Delta H_r^\circ = [6 \times \Delta H_f^\circ(\text{CO}_2(\text{g})) + 6 \times \Delta H_f^\circ(\text{H}_2\text{O}(\text{g}))] - [1 \times \Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6 \times \Delta H_f^\circ(\text{O}_2(\text{g}))]$$

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

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

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

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

Entropy Changes and the Equilibrium State

➤ $\Delta S_{\text{univ}} > 0 \rightarrow$ the forward reaction is spontaneous

➤ $\Delta S_{\text{univ}} < 0 \rightarrow$ the forward reaction is non-spontaneous (the reverse reaction is spontaneous)

➤ $\Delta S_{\text{univ}} = 0 \rightarrow$ the reaction is at equilibrium

$$\Rightarrow \text{At equilibrium: } \Delta S_{\text{univ}}^\circ = \Delta S_{\text{sys}}^\circ - \Delta H_{\text{sys}}^\circ/T = 0$$

$$\Rightarrow \text{At equilibrium: } \Delta S_{\text{sys}}^\circ = \Delta H_{\text{sys}}^\circ/T$$

→ 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 $\Delta S_{\text{vap}}^\circ$ of H_2O at its normal b.p.

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

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

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

20.3 Entropy, Free Energy and Work

– **Gibbs free energy** (G) – a state function defined as: $G = H - TS$

Free Energy Change and Spontaneity

➤ From the 2nd law at constant T and P ,

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \Rightarrow \Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

\rightarrow Multiply the equation by $(-T)$

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

$$\Delta H_{sys} - T\Delta S_{sys} = (H_f - H_i)_{sys} - T(S_f - S_i)_{sys} =$$

$$= (H_f - TS_f)_{sys} - (H_i - TS_i)_{sys} = (G_f - G_i)_{sys} = \Delta G_{sys}$$

$$\Rightarrow \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} = -T\Delta S_{univ}$$

\Rightarrow At constant T and P , the entropy change of the universe is related to the free energy change of the system $\rightarrow -T\Delta S_{univ} = \Delta G_{sys}$

\rightarrow If $\Delta S_{univ} > 0 \Rightarrow -T\Delta S_{univ} < 0 \Rightarrow \Delta G_{sys} < 0$

$\Rightarrow \Delta G_{sys} < 0 \rightarrow$ a **criterion for spontaneity** in any system at constant T and P

- $\Delta G_{sys} < 0 \rightarrow$ the forward reaction is spontaneous
 - $\Delta G_{sys} > 0 \rightarrow$ the forward reaction is non-spontaneous (the reverse reaction is spontaneous)
 - $\Delta G_{sys} = 0 \rightarrow$ the reaction is at equilibrium
- \rightarrow For simplicity, the subscript sys can be omitted from all state functions related to the system, so at const. T and P
- $$\Delta G = \Delta H - T\Delta S$$

The Effect of Temperature on ΔG

- ΔG depends strongly on T
 - Use the symbol $\Delta G^T \rightarrow$ for temperature T
- ΔH and ΔS depend very little on T
 - ΔH and ΔS can be assumed independent of T
 - $\Rightarrow \Delta G^T = \Delta H - T\Delta S$
- The sign of ΔG^T depends on the signs of ΔH and ΔS and the magnitude of T

ΔH	ΔS	ΔG^T		Spontaneous?
		High T	Low T	
–	+	–	–	Yes at all T s
–	–	+	–	No at high T s; Yes at low T s
+	+	–	+	Yes at high T s; No at low T s
+	–	+	+	No at all T s

\Rightarrow If ΔH and ΔS have the same sign, ΔG^T can be positive or negative depending on the value of T

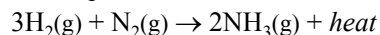
- At a certain T , the system reaches equilibrium
- $\Rightarrow \Delta G^T = 0 \rightarrow \Delta H - T\Delta S = 0 \rightarrow \Delta H = T\Delta S$
- $\Rightarrow T = \Delta H / \Delta S \leftarrow T$ at which equilibrium is reached
- At any other T , the system is not at equilibrium, and the process either is or isn't spontaneous
- The T -range at which the process is spontaneous, can be found from

$$\Delta G^T < 0 \rightarrow \Delta H - T\Delta S < 0 \rightarrow \Delta H < T\Delta S$$

\rightarrow Solving for T gives the desired T -range

Note: Multiplying or dividing with a $(-)$ number changes $(<)$ to $(>)$

Example: Is the following reaction spontaneous at high or low temperatures?



Exothermic reaction $\Rightarrow \Delta H < 0$

Less gaseous products $\Rightarrow \Delta S < 0$

$$\Delta G^T = \Delta H - T\Delta S = (-) - T(-) = (-) + T(+) < 0 \text{ at } \underline{\text{low } T}$$

Example: For the same reaction at certain conditions, $\Delta H = -91.8 \text{ kJ}$ and $\Delta S = -197 \text{ J/K}$. What is the T -range at which the reaction is spontaneous?

$$\Delta G^T = \Delta H - T\Delta S < 0 \rightarrow \Delta H < T\Delta S$$

$$-91.8 \text{ kJ} < T(-0.197 \text{ kJ/K}) \leftarrow \text{Multiply by } (-1)$$

$$91.8 \text{ kJ} > T(0.197 \text{ kJ/K}) \leftarrow \text{Note: } (<) \text{ flips to } (>)$$

$$T < 91.8 \text{ kJ} / 0.197 \text{ kJ/K} \Rightarrow \underline{T < 466 \text{ K}} \leftarrow T\text{-range}$$

Standard Free Energy Changes

- **Standard free energy of reaction ($\Delta G_r^{\circ,T}$)** – the free energy change for a reaction in which all reactants and products are present in their standard states at a specified temperature T
- **Standard free energy of formation ($\Delta G_f^{\circ,T}$)** – the standard free energy for the reaction of formation of 1 mol of a substance from its elements at a specified temperature T (usually 298 K)

$$\Delta G_r^{\circ,T} = \sum m \Delta G_f^{\circ,T}(\text{products}) - \sum n \Delta G_f^{\circ,T}(\text{reactants})$$

→ $\Delta G_f^{\circ,298}$ values are given in Appendix B

⇒ The equation can be used to calculate $\Delta G_r^{\circ,298}$ for a reaction (**only for 298 K!**)

→ At any other temperature ($T \neq 298 \text{ K}$), $\Delta G^{\circ,T}$ is calculated from the equation

$$\Delta G^{\circ,T} = \Delta H^{\circ} - T\Delta S^{\circ}$$

Example: Calculate the standard free energy for the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ at (a) **298 K** and (b) **1500 K**

$$\begin{aligned} \text{a) } \Delta G_r^{\circ,298} &= 2 \times \Delta G_f^{\circ,298}(\text{SO}_3(\text{g})) - \\ &\quad - [2 \times \Delta G_f^{\circ,298}(\text{SO}_2(\text{g})) + 1 \times \Delta G_f^{\circ,298}(\text{O}_2(\text{g}))] = \\ &= 2(-371) - [2(-300) + 1(0)] = \boxed{-142 \text{ kJ}} \end{aligned}$$

$$\Rightarrow \Delta G_r^{\circ,298} < 0$$

⇒ The reaction is **spontaneous** at standard conditions and **298 K**

b) No data for $\Delta G_f^{\circ,1500} \Rightarrow$ use $\Delta G^{\circ,T} = \Delta H^{\circ} - T\Delta S^{\circ}$

$$\begin{aligned} \rightarrow \Delta H_r^{\circ} &= 2 \times \Delta H_f^{\circ}(\text{SO}_3(\text{g})) - \\ &\quad - [2 \times \Delta H_f^{\circ}(\text{SO}_2(\text{g})) + 1 \times \Delta H_f^{\circ}(\text{O}_2(\text{g}))] = \\ &= 2(-396) - [2(-297) + 1(0)] = \boxed{-198 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \rightarrow \Delta S_r^{\circ} &= 2 \times S^{\circ}(\text{SO}_3(\text{g})) - [2 \times S^{\circ}(\text{SO}_2(\text{g})) + 1 \times S^{\circ}(\text{O}_2(\text{g}))] = \\ &= 2(257) - [2(248) + 1(205)] = \boxed{-187 \text{ J/K}} \end{aligned}$$

$$\begin{aligned} \rightarrow \Delta G_r^{\circ,1500} &= -198 \text{ kJ} - 1500 \text{ K} \times (-0.187 \text{ kJ/K}) = \\ &= -198 \text{ kJ} + 281 \text{ kJ} = \boxed{+83 \text{ kJ}} \end{aligned}$$

$$\Rightarrow \Delta G_r^{\circ,1500} > 0$$

⇒ The reaction is **not spontaneous** at standard conditions and **1500 K**

ΔG and the Work a System Can Do

➤ ΔG is equal to the **maximum work obtainable** from a system in which a spontaneous process takes place
→ $\Delta G = w_{\text{max}}$

➤ ΔG is also equal to the minimum work that must be done in order to reverse a spontaneous process

➤ To obtain the maximum work from a system, the process must be carried out **reversibly**

➤ **Reversible processes** are carried out through infinitely small steps (infinitely slow)

➤ Can be reversed without leaving permanent changes in the system or its surroundings

➤ The system is in an “almost equilibrium” state during such processes

➤ When work is done reversibly, the driving force of the process exceeds the opposing force by an infinitely small amount so the process is extremely slow

➤ **Real processes** are not reversible because they are carried out faster in a limited number of steps

➤ The work obtained from real processes is less than the maximum work (less than ΔG)

➤ The unharnessed portion of the free energy (ΔG) is lost to the surroundings as heat

⇒ In real processes, one must compromise between the speed and amount of work (free energy) gained from the process

20.4 Free Energy, Equilibrium, and Reaction Direction

➤ The direction of reaction can be predicted from the sign of ΔG or by comparing Q and K

➤ If $Q < K \rightarrow Q/K < 1 \rightarrow \ln Q/K < 0$ and $\Delta G < 0$, the forward reaction proceeds

➤ If $Q > K \rightarrow Q/K > 1 \rightarrow \ln Q/K > 0$ and $\Delta G > 0$, the reverse reaction proceeds

➤ If $Q = K \rightarrow Q/K = 1 \rightarrow \ln Q/K = 0$ and $\Delta G = 0$, the reaction is at equilibrium

⇒ ΔG and $\ln Q/K$ have the same signs and are related:

$$\Delta G_r^T = RT \ln \frac{Q}{K} = RT \ln Q - RT \ln K$$

⇒ ΔG_r is concentration dependent (depends on Q)
 ⇒ ΔG_r can be viewed as a difference between the free energy of the system at the current concentrations of reactants and products, Q , and that at equilibrium, K

➤ At standard-state conditions, all concentrations and pressures are equal to 1, so $Q = 1$ and $\Delta G_r = \Delta G_r^\circ$

$$\Rightarrow \Delta G_r^{\circ,T} = RT \ln 1 - RT \ln K = 0 - RT \ln K$$

$$\Delta G_r^{\circ,T} = -RT \ln K$$

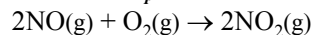
→ The equation is used to calculate ΔG° from K and vice versa

➤ If $K > 1 \rightarrow \Delta G^\circ < 0 \rightarrow$ products are favored at equilibr.

➤ If $K < 1 \rightarrow \Delta G^\circ > 0 \rightarrow$ reactants are favored at equilibr.

➤ If $K = 1 \rightarrow \Delta G^\circ = 0$

Example: Calculate K_p at 298 K for the reaction



→ Calculate $\Delta G_r^{\circ,298}$

→ $T = 298 \text{ K} \Rightarrow \Delta G_f^{\circ,298}$ values from Appendix B can be used

$$\begin{aligned} \Delta G_r^{\circ,298} &= 2 \times \Delta G_f^{\circ,298}(\text{NO}_2\text{(g)}) - \\ &\quad - [2 \times \Delta G_f^{\circ,298}(\text{NO(g)}) + 1 \times \Delta G_f^{\circ,298}(\text{O}_2\text{(g)})] = \\ &= 2(+51.3) - [2(+86.6) + 1(0)] = -70.6 \text{ kJ/mol} \end{aligned}$$

$$\Delta G_r^{\circ,T} = -RT \ln K \Rightarrow \ln K = -\Delta G_r^{\circ,T} / RT$$

$$K = e^{\frac{-\Delta G_r^{\circ,T}}{RT}} = e^{\frac{-(-70.6 \text{ kJ/mol})}{8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K} \times 298 \text{ K}}} = 2.4 \times 10^{12} = K_p$$

$K_p \gg 1 \Rightarrow$ the products are highly favored

➤ Combining $\Delta G_r^T = RT \ln Q - RT \ln K$ with $\Delta G_r^{\circ,T} = -RT \ln K$ leads to:

$$\Delta G_r^T = \Delta G_r^{\circ,T} + RT \ln Q$$

→ The equation is used to calculate ΔG_r^T for any nonstandard state from $\Delta G_r^{\circ,T}$ for the respective standard state both at temperature, T , and the reaction quotient of the nonstandard state, Q

→ $\Delta G_r^{\circ,T}$ is calculated as $\Delta G_r^{\circ,T} = \Delta H_r^\circ - T\Delta S_r^\circ$

→ $R = 8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}$

→ T is the same for all quantities in the equation

⇒ ΔG_r^T is associated with a certain composition (Q) and a certain temperature (T)

Example: Calculate the free energy change for the reaction $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightarrow 2\text{HI(g)}$ at 500 K if the partial pressures of H_2 , I_2 , and HI are 1.5, 0.88 and 0.065 atm, respectively.

→ Nonstandard state at 500 K ($\Delta G_r^{500} = ?$)

→ Calculate $\Delta G_r^{\circ,500}$ as $\Delta G_r^{\circ,T} = \Delta H_r^\circ - T\Delta S_r^\circ$

$$\begin{aligned} \rightarrow \Delta H_r^\circ &= 2 \times \Delta H_f^\circ(\text{HI(g)}) - \\ &\quad - [1 \times \Delta H_f^\circ(\text{H}_2\text{(g)}) + 1 \times \Delta H_f^\circ(\text{I}_2\text{(g)})] = \\ &= 2(+25.9) - [1(0) + 1(+62.4)] = -10.6 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \rightarrow \Delta S_r^\circ &= 2 \times S^\circ(\text{HI(g)}) - [1 \times S^\circ(\text{H}_2\text{(g)}) + 1 \times S^\circ(\text{I}_2\text{(g)})] = \\ &= 2(206) - [1(131) + 1(261)] = +20 \text{ J/K} \end{aligned}$$

$$\rightarrow \Delta G_r^{\circ,500} = -10.6 \text{ kJ} - 500 \text{ K} \times (0.020 \text{ kJ/K}) = -20.6 \text{ kJ}$$

$$Q_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}} = \frac{(0.065)^2}{1.5 \times 0.88} = 3.2 \times 10^{-3}$$

$$\begin{aligned} \Delta G_r^{500} &= \Delta G_r^{\circ,500} + R \times 500 \text{ K} \times \ln Q \\ &= -20.6 \frac{\text{kJ}}{\text{mol}} + 8.314 \times 10^{-3} \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \times 500 \text{ K} \times \ln(3.2 \times 10^{-3}) \end{aligned}$$

$$= -20.6 \frac{\text{kJ}}{\text{mol}} - 23.9 \frac{\text{kJ}}{\text{mol}}$$

$$\Rightarrow \Delta G_r^{500} = -44.5 \frac{\text{kJ}}{\text{mol}}$$

$$\Rightarrow \Delta G_r^{500} < 0$$

⇒ The reaction is spontaneous at this nonstandard state and 500 K

Deriving the van't Hoff Equation

➤ The van't Hoff equation gives the temperature dependence of the equilibrium constant

$$\begin{aligned} \Delta G_r^{\circ,T} &= -RT \ln K \\ \Delta G_r^{\circ,T} &= \Delta H_r^\circ - T\Delta S_r^\circ \end{aligned} \quad \left| \quad -RT \ln K = \Delta H_r^\circ - T\Delta S_r^\circ \right.$$

$$-\ln K = \frac{\Delta H_r^\circ}{RT} - \frac{\Delta S_r^\circ}{R}$$

➤ If the equation is applied for two different T s, and ΔH_r° and ΔS_r° are assumed independent of T

$$\rightarrow \ln \frac{K_2}{K_1} = -\frac{\Delta H_r^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

