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,

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

→ Multiply the equation by ($-T$)

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

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

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

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

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

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

$\Rightarrow \boxed{\Delta G_{sys} < 0} \rightarrow$ 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

→ 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 Ts
–	–	+	–	No at high Ts; Yes at low Ts
+	+	–	+	Yes at high Ts; No at low Ts
+	–	+	+	No at all Ts

⇒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
  $\Rightarrow \Delta G^T = 0 \quad \rightarrow \quad \Delta H - T\Delta S = 0 \quad \rightarrow \quad \Delta H = T\Delta S$
  $\Rightarrow T = \Delta H/\Delta S \leftarrow T$ 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

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

→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?

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g) + heat$$
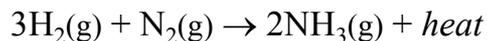
Exothermic reaction $\Rightarrow \Delta H < 0$

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

$\Delta G^T = \Delta H - T\Delta S = (-) - T(-) = (-) + T(+) < 0$ at **low** T

Example: For the same reaction at certain conditions, ΔH = -91.8 kJ and ΔS = -197 J/K. What is the T-range at which the reaction is spontaneous?

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

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

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

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

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Standard Free Energy Changes
- **Standard free energy of reaction** $(\Delta G_r^{o,T})$ – 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** $(\Delta G_f^{o,T})$ – 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)

$\boxed{\Delta G_r^{o,T} = \Sigma m \Delta G_f^{o,T}(\textbf{products}) - \Sigma n \Delta G_f^{o,T}(\textbf{reactants})}$

$\rightarrow \Delta G_f^{o,298}$ values are given in Appendix B

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

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

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

Example: Calculate the standard free energy for the reaction $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ at **(a) 298 K** and **(b) 1500 K**

a) $\Delta G_r^{o,298} = 2 \times \Delta G_f^{o,298}(SO_3(g)) -$
$\qquad - [2 \times \Delta G_f^{o,298}(SO_2(g)) + 1 \times \Delta G_f^{o,298}(O_2(g))] =$
$= 2(-371) - [2(-300) + 1(0)] = \boxed{-142\ \text{kJ}}$

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

$\Rightarrow$ The reaction **is spontaneous** at standard conditions and **298 K**

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

$\rightarrow \Delta H_r^o = 2 \times \Delta H_f^o(SO_3(g)) -$
$\qquad\qquad - [2 \times \Delta H_f^o(SO_2(g)) + 1 \times \Delta H_f^o(O_2(g))] =$
$= 2(-396) - [2(-297) + 1(0)] = \textbf{-198 kJ}$

$\rightarrow \Delta S_r^o = 2 \times S^o(SO_3(g)) - [2 \times S^o(SO_2(g)) + 1 \times S^o(O_2(g))] =$
$= 2(257) - [2(248) + 1(205)] = \textbf{-187 J/K}$

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

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

$\Rightarrow$ 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 → $\Delta G = w_{max}$

➢ 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