

THERMODYNAMICS AND EQUILIBRIUM

- A spontaneous reaction is one that occurs without continuous outside assistance, proceeding to completion in open systems
 - Spontaneous reactions can be either exothermic (sodium + water) or endothermic (dissolving ammonium nitrate)
 - Most exothermic reactions ($\Delta H < 0$) are spontaneous and most endothermic reactions ($\Delta H > 0$) are non-spontaneous
 - There is a natural tendency to minimize energy
- Entropy (S) is a measure of disorder or randomness
 - There is a natural tendency to maximize randomness
 - Entropy increases when randomness increases
 - $\Delta S = S_{\text{products}} - S_{\text{reactants}}$
 - if $\Delta S > 0$, then the products are more random than the reactants
 - if $\Delta S < 0$, then the products are more ordered (less random) than the reactants
- an increase in entropy is seen if:
 - the volume of a gaseous system increases
 - particles can spread out more
 - the temperature of the system increases
 - particles are moving faster
 - $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$
 - Solid particles are close together; gas particles are able to spread out
 - There are more product particles made than there were reactant particles
 - $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$
 - A complex molecule is broken down into simpler substances
 - $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$

Free Energy and Equilibrium

- Free energy (Gibbs free energy) means available energy to do useful work
- $\Delta G = \Delta H - T\Delta S$ where ΔG = change in free energy (kJ), ΔH = change in enthalpy (kJ), T = temperature (K) and ΔS = change in entropy (kJ/K)

- the value of ΔG tells us whether the reaction is a source of useful energy that can be converted into another form (mechanical, electrical, etc)
- it also will tell us if a reaction is spontaneous and how temperature affects the direction of the reaction
 - when ΔG is negative, the forward reaction is spontaneous
 - when ΔG is positive, the forward reaction is non-spontaneous; the reverse reaction is spontaneous
 - when ΔG is 0, the reaction is at equilibrium

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Comments
-	+	$\Delta G = (-) - T(+)$	ΔH favourable; ΔS favourable Spontaneous reaction at all temperatures
-	-	$\Delta G = (-) - T(-)$	ΔH favourable; ΔS not favourable Spontaneous reaction only at low temperatures
+	-	$\Delta G = (+) - T(-)$	ΔH and ΔS not favourable Non-spontaneous reaction at all temperatures
+	+	$\Delta G = (+) - T(+)$	ΔH not favourable; ΔS favourable Spontaneous reaction only at high temperatures

- before any reaction can begin, E_a must be supplied and surpassed
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ refers to the standard state at 298 K
 - $\Delta H^\circ = \sum \Delta H^\circ_f \text{ products} - \sum \Delta H^\circ_f \text{ reactants}$ (Hess' Law)
 - $\Delta S^\circ = \sum \Delta S^\circ \text{ products} - \sum \Delta S^\circ \text{ reactants}$