

7.2 Thermodynamics and Equilibrium

- Enthalpy → heat → H
- Entropy → disorder (randomness) → S
- Favourable Change: the change that has a natural tendency to happen under certain conditions.

Enthalpy and Favourable Changes

- Energy is the key.
- Exothermic reactions are usually favoured because they release energy and the products are at a lower energy state. Secondly, the released energy can be used to further propagate the reaction.
- Endothermic reactions can also be favoured but certain conditions must be met. There needs to be a substantial increase in entropy that forces the reaction to take place.

Temperature and Favourable Changes

- $\text{Hg}_{(l)} + \frac{1}{2} \text{O}_{2(g)} \leftrightarrow \text{HgO}_{(s)} \quad \Delta H = -90.8 \text{ kJ}$
Below 400°C the exothermic reaction is favoured
Above 400°C the endothermic reaction is favoured
- Sometimes reactions just take place and are not dependent on enthalpy. See figure 7.5 where entropy is the driving force that makes a change take place.

Entropy and Favourable Changes

- Entropy is the tendency toward randomness or disorder in a system. It is also a thermodynamic property that can be measured.
- Usually, the lower the temperature of a substance then the lower the entropy. As it is heated the particles become more energetic and move faster and become more chaotic which increases the entropy.
- Second Law of Thermodynamics: The entropy (or the tendency toward randomness) of the universe is constantly increasing. $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$
- Heat tends to drive exothermic reactions and entropy tends to drive endothermic reactions.
- An increase in entropy through the formation of products drives the reaction.
- What causes an increase in entropy?
 1. A reaction when a gas is formed from a solid.
 2. A reaction when is gas is evolved from a solution.
 3. A reaction where the number of gaseous product is greater than the number of moles of gaseous reactant.
 4. A reaction where crystals dissolve in water.

Free Energy and Equilibrium

- $\Delta G = \Delta H - T\Delta S$ (change in free energy = change in enthalpy – temperature (K) × change in entropy)
- Free energy is available energy that can be used to do work.
- The calculation of free energy (G) can be used to predict the probable spontaneity of a reaction.
 - When ΔG is negative, the forward reaction is favoured.
 - When ΔG is zero, the reaction is at equilibrium.
 - When ΔG is positive, the reverse reaction is favoured.
- In the case of $\text{Hg}_{(l)} + \frac{1}{2} \text{O}_{2(g)} \leftrightarrow \text{HgO}_{(s)}$ $\Delta H = -90.8 \text{ kJ}$ from the example above:
 - Below 400°C the exothermic reaction is favoured because $-T\Delta S$ is not large enough to force the reverse reaction since it is small than ΔH . This forces the product to have less entropy (gas to solid)
 - Above 400°C the endothermic reaction is favoured because $-T\Delta S$ is large enough to force the reverse reaction since it is greater than ΔH . This forces the product to have greater entropy (solid to gas)
 - At this point you are asking, why? The reason is the temperature. T times ΔS

- Table 7.1 (you will need this)

ΔH	ΔS	$-T\Delta S$	Results
-	+	-	Both ΔH and ΔS favour the forward reaction.
+	-	+	Neither ΔH and ΔS favour the forward reaction.
-	-	+	ΔH is favourable and ΔS not favourable to the forward reaction. The reaction will likely go forward at low temperatures.
+	+	-	ΔH is not favourable and ΔS favourable to the forward reaction. The reverse reaction will likely go forward at high temperatures.

Homework

- Read 7.2 and answer all questions.