

AP Chemistry Ch.17 Thermodynamics Section 1 (17.1 to 17.4)

*The First Law of Thermodynamics is the Law of Conservation of Energy: **Energy can neither be created nor destroyed—the total energy of the universe is constant.**

Energy can be transformed and interchanged by physical and chemical processes but the total energy is constant.

Spontaneous Processes and Entropy

A spontaneous process is a process that occurs without outside intervention.
(It tells us nothing about the speed of the process.)

With Enthalpy, an **exothermic** reaction occurs spontaneously.
But **endothermic** processes can also occur spontaneously such as ice melting and water evaporating.

The other piece of the thermodynamic process is **Entropy**.
Entropy is the measure of molecular randomness or disorder. Entropy (S)

The driving force for a spontaneous process is an increase in the entropy of the universe (S_{univ}).

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$

Nature gravitates toward randomness. The overall randomness of the universe is destined for the universal death of order.

Since entropy is a measure of molecular randomness or disorder, then entropy of S < l < g and the entropy of a solid crystal < entropy of aqueous ions of the crystal in solution.

Entropy is a thermodynamic function that describes the number of arrangements (positions and/or energy levels) that are available to a system in a given state. (Microstates)

Nature spontaneously proceeds toward states that have the highest probability of existing or more microstates consistent with disorder. (See p. 792) This is called positional probability.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

*The Second Law of Thermodynamics states: **In any spontaneous process, there is always and increase in the entropy of the universe.**

The total energy (enthalpy) of the universe is constant, and the (entropy) of the universe is increasing.

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$

If ΔS_{univ} is (-), the process is spontaneous in the opposite direction.

The entropy changes in the surroundings (ΔS_{surr}) are primarily determined by the direction of the heat flow.

Exothermic processes increase ΔS_{surr} because the heat flows to the surroundings increasing the random motion of the surroundings.

Therefore, an exothermic process is an important driving force for spontaneity.

The significance of an exothermic driving force depends on the temperature of the process.

***The impact of a given quantity of energy as heat going to or coming from the surroundings will be greater at lower temperatures.**

(P. 796)

- 1) The sign of ΔS_{surr} depends on the direction of the heat flow at constant temperatures. In exothermic processes, heat flows to the surroundings increasing its randomness and vs/vr for endothermic processes.
- 2) The magnitude of ΔS_{surr} depends on temperature. The transfer of a given amount of energy as heat has a greater percent change in randomness if the temperature of the surroundings is low than if it is high.

The tendency of a system to go to lower energy is dependent on the temperature.

Driving Force provided
By energy flow (heat) = magnitude of the entropy
change of the surroundings = $\frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$

Exothermic Process $\Delta S_{\text{surr}} = \frac{+ \text{quantity of heat (J)}}{\text{Temperature (K)}}$

Endothermic Process $\Delta S_{\text{surr}} = \frac{- \text{quantity of heat (J)}}{\text{Temperature (K)}}$

(From Chapter 6) Heat flow (constant P) = change in enthalpy = ΔH

Combining the two concepts: $\Delta S_{\text{surr}} = \frac{-\Delta H}{T}$

So if ΔH is negative (exothermic), then ΔS_{surr} will be positive.

If ΔH is positive (endothermic), then ΔS_{surr} will be negative.

The value of ΔS will be in Joules and must be converted to kJ when used with ΔH .

Example bottom of (p.797)

Please note Table 17.13 (p.798) for spontaneous and nonspontaneous situations.

Free Energy (Gibbs Free Energy) (G)

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

(When using this equation, ΔS is given in J and ΔH and ΔG are given in kJ. Change J to kJ when plugging in.)

Manipulation of the equation results in

$$\Delta S_{\text{univ}} = \frac{-\Delta G}{T} \text{ (at constant T and P)}$$

This means that the entropy of the universe is only positive (+) when ΔG is negative (-). For a process to be spontaneous, **ΔG must be negative (-)**.

(p. 800, Table 17.5) very important.

ΔH	ΔS	ΔG
+	+	Spontaneous at High temp.
-	+	Spontaneous at All temp.
-	-	Spontaneous at Low temp.
+	-	Spontaneous at No temp. or Nonspontaneous at All temp.

When finding the temperature at which a system is spontaneous, we must find the temperature at which ΔG^0 is negative. We also know that when $\Delta G^0 = 0$ the system is at equilibrium and is neither spontaneous nor nonspontaneous.

By making $\Delta G^0 = 0$ and solving for T, we can find the temperature above or below which ΔG^0 is negative.

(See example on p. 301. In the example, both ΔH and ΔS are positive so it would be spontaneous at high temp, so we would assume that the reaction is spontaneous at temperatures **higher** than the value of T.)