- **<u>Chapter 10: Energy</u>**

- SECOND LAW OF THERMODYNAMICS:
  - The entropy of the Universe increases during any **spontaneous** process.
    - Spontaneous: the process proceeds on its own, without the need for an input of energy.

- THE ENTROPY:
  - it is a measure of how disordered a system is
  - When a system becomes more disordered, its entropy will increase
  - An increase in entropy means that the system becomes energetically more stable
  - For example, during the thermal decomposition of calcium carbonate ($CaCO_3$) the entropy of the system increases:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

  - In this decomposition reaction, a gas molecule (CO_2) is formed
  - The CO_2 gas molecule is more disordered than the solid reactant ($CaCO_3$), as it is constantly moving around
  - As a result, the system has become more disordered and there is an increase in entropy
  - if the number of gaseous molecules in a reaction changes, there will also be a change in entropy
  - The greater the number of gas molecules, the greater the number of ways of arranging them, and thus the greater the entropy
  - For example the decomposition of calcium carbonate ($CaCO_3$)

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

  - The CO_2 gas molecule is more disordered than the solid reactant ($CaCO_3$) as it can freely move around whereas the particles in $CaCO_3$ are in fixed positions in which they can only slightly vibrate
  - The system has therefore become more disordered and there is an increase in entropy

- Similarly, a decrease in the number of gas molecules results in a decrease in entropy causing the system to become less energetically stable
- For example, the formation of ammonia in the Haber process

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$$

  - In this case, all of the reactants and products are gasses
  - Before the reaction occurs, there are four gas molecules (1 nitrogen and 3 hydrogen molecules) in the reactants
  - After the reaction has taken place, there are now only two gas molecules (2 ammonia molecules) in the products
  - Since there are fewer molecules of gas in the products, there are fewer ways of arranging the energy of the system over the products
  - The system has become more ordered causing a decrease in entropy
  - The reactants (N_2 and H_2) are energetically more stable than the product (NH_3)

- ENTROPY FORMULA:

$$\Delta S = \frac{q_{rev}}{T} \qquad (1)$$

where S is the entropy, q_{rev} is the heat transferred, and T is the *thermodynamic* temperature,

- Rev means that the heat is transferred reversibly.
- the system was at all times in equilibrium.

- COMMON ALPHABETS:

- SECOND LAW THERMODYNAMICS MATHEMATICAL:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

- FIRST LAW THERMODYNAMICS:
    - The first law of thermodynamics states that the energy of the universe is constant.
    - The change in the internal energy of a system is the sum of the heat transferred and the work done.
    - The heat flow is equal to the change in the internal energy of the system plus the PV work done.

$$\underbrace{\Delta U_{sys} = q + w}_{\text{First Law of Thermodynamics}}$$

- STANDARD STATE:

The most stable form of a pure element at 25ºC and 105 Pa.

- STATE FUNCTIONS: a property whose value does not depend on the path taken to reach that specific value. Example: temperature, pressure, density, volume, Gibb's energy, potential energy, enthalpy, **internal energy,** and entropy.
- PATH FUNCTIONS: properties or quantities whose values depend on the transition of a system from the initial state to the final state. The two most common path functions are **heat and work.**

❖ CLOSED VS ISOLATED SYSTEM:

- In an isolated system no heat is exchanged with the surroundings
- In a closed system heat may pass the boundaries.

$$\Delta U = 0 \ \ \text{Isolated System}$$

$$\Delta U = q + w \quad \text{Closed System}$$

- q is heat transferred into the system
- w is work done on the system
- U is change in internal energy
- IT IS IMPOSSIBLE TO DETERMINE THE ABSOLUTE VALUE OF INTERNAL ENERGY

❖ ENTHALPY

   ➢ The enthalpy change is just the heat supplied (or absorbed) by a reaction, when we account for the work done in pushing back the atmosphere.

$$\Delta H = \Delta U + P\Delta V$$

- GIBBS ENERGY:
  - The Gibbs free energy (G) is the energy change that takes into account both the entropy change of a reaction and the enthalpy change
  - The Gibbs equation is:

ΔG□ = ΔHreaction□ - TΔSsystem□

- The units of ΔG□ are in kJ mol-1
- The units of ΔHreaction□ are in kJ mol-1
- The units of T are in K
- The units of ΔSsystem□ are in J K-1 mol-1 (and must therefore be converted to kJ K-1 mol-1 by dividing by 1000)

$$\Delta S_{system} + \Delta S_{surroundings} > 0$$

$$\Delta S_{surroundings} = \frac{q_{surroundings}}{T}$$

$$q_{surroundings} = -q_{system}$$

$$\Delta S_{surroundings} = \frac{-q_{system}}{T}$$

$$\Delta S_{system} + \frac{-q_{system}}{T} > 0$$

$$T\Delta S_{system} - q_{system} > 0$$

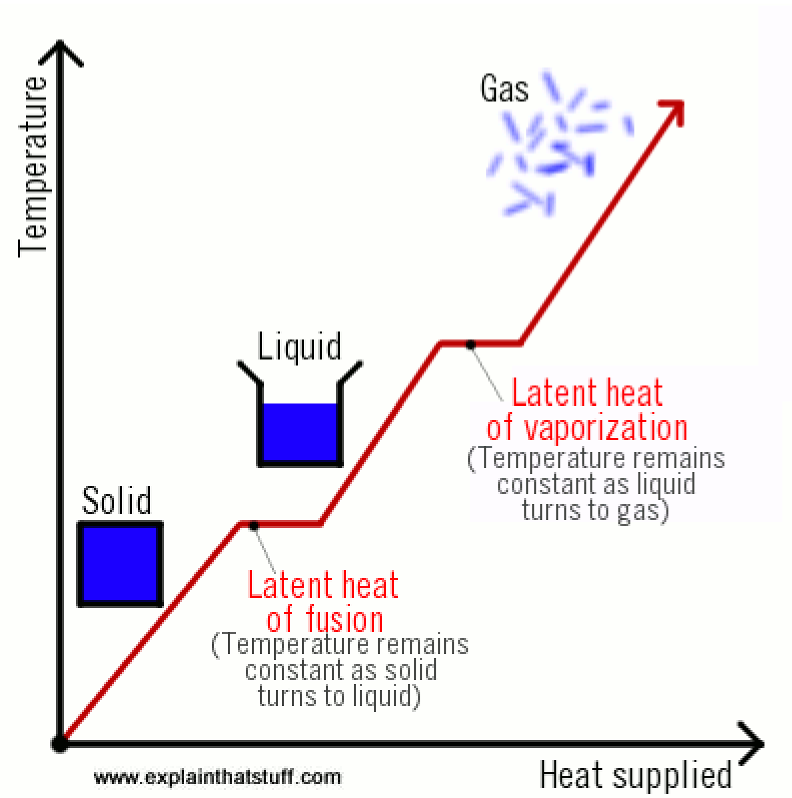
$$T\Delta S_{system} - \Delta H_{system} > 0$$

$$\Delta H_{system} - T\Delta S_{system} < 0$$

This means that when Gibbs energy decreases, it is just another way of saying that the entropy increased, specifically $\Delta G = -T\Delta S_{universe}$.

- **-ve G and +ve S means spontaneous**
- A reaction with a **positive** enthalpy change and a **positive** entropy change will be spontaneous under **high** temp
- A reaction with a **positive** enthalpy change and a **negative** entropy change will **NEVER** be spontaneous
- A reaction with a **negative** enthalpy change and a **negative** entropy change will be spontaneous under **low** temp

- **ENTHALPY OF FUSION:** the amount of energy that must be supplied to a **solid** substance (typically in the form of heat) in order to trigger a change in its physical state and convert it **into** a **liquid** (when the pressure of the environment is kept constant).
- **ENTHALPY OF VAPORIZATION:** the amount of energy (enthalpy) that must be added to a **liquid** substance, to transform a quantity of that substance into a **gas**.



$$q = mc\Delta T$$