
The Second Law of Thermo

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Ron Robertson

I. Types of changes

- **Spontaneous - have a natural tendency to occur**
- **Nonspontaneous - have no tendency to occur**
- **The terms spontaneous and nonspontaneous have nothing to do with reaction rate; these terms answer the question “can it occur?” with no regard to the time required.**
- **The property of matter which determines spontaneity is called ENTROPY.**

II. Entropy

- Entropy describes the number of ways that energy can be stored in system and is related to disorder.
- Molecular energy is quantized and can be stored in several ways with the following energy level spacings:

Translational (10^{-37} J), Vibrational (10^{-20} J),
Rotational (10^{-22} J), Electronic (10^{-19} J)

Ways to change energy storage:

1. change energy level spacings
(expansion/contract gas, phase change)
2. change amount of internal energy (change T)

Changing energy level spacings

Expansion of gas

Change in translational energy levels, the energy levels get closer together so more ways to store energy

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Phase Change

As we go from solid to liquid we pick up rotational and translational modes which have closely spaced energy levels. This increases entropy.

As we go from liquid to gas we pick up more closely spaced translational energy levels as a result of the expansion. This also increases entropy.

In general breaking bonds that confine molecules or atoms causes an increase in rotational and translational modes so that entropy increases.

Changing the amount of energy

At the temperature increases the amount of energy to be distributed increases and thus the number of ways to distribute the energy.

The 2nd Law of Thermo

The 2nd law of thermodynamics says that the entropy of an isolated system increases in a spontaneous change. Entropy is a state property.

We can define entropy as

$$dS = dq_{rev}/T$$

so

$$\Delta S = \int dS = \int \frac{dq_{rev}}{T}$$

For isothermal systems we can measure an entropy change as

$$\Delta S = \frac{q_{rev}}{T} \quad \text{Entropy thus has units of J/K}$$

For an isothermal process we know that $DU = 0$ and that $q = -w$.

We also know that $w = -nRT \ln V_f/V_i$ if the process is reversible. This means that $q = +nRT \ln V_f/V_i$.

This gives an expression for DS :

$$DS = +nR \ln V_f/V_i$$

- **For constant V**

$$dq = C_v dT$$

$$\text{This gives } DS = C_v \ln T_f/T_i$$

- **For constant P**

$$dq = C_p dT$$

$$\text{This gives } DS = C_p \ln T_f/T_i$$