

2nd Law of Thermodynamics

The second law is concerned with entropy, which is a measure of disorder. The second law says that the entropy of the universe increases

There are two classical statements of the second law of thermodynamics:

Kelvin & Planck

"No (heat) engine whose working fluid undergoes a cycle can absorb heat from a single reservoir, deliver an equivalent amount of work, and deliver no other effect"

Clausius

"No machine whose working fluid undergoes a cycle can absorb heat from one system, reject heat to another system and produce no other effect"

Both statements of the second law place constraints on the first law by identifying that energy goes downhill.

The second law is concerned with **entropy (S)**, which is a measure of disorder. The second law says that the entropy of the universe increases. An increase in overall disorder is therefore spontaneous. If the volume and energy of a system are constant, then every change to the system increases the entropy. If volume or energy change, then the entropy of the system actually decrease. However, the entropy of the universe does not decrease.

For energy to be available there must be a region with high energy level and a region with low energy level. Useful work must be derived from the energy that would flows from the high level to the low level.

- **100% of the energy can not be transformed to work**
- **Entropy can be produced but never destroyed**

Efficiency of a heat machine

The efficiency of a heat machine working between two energy levels is defined in terms of absolute temperature:

$$\eta = (T_h - T_c) / T_h = 1 - T_c / T_h(1)$$

where

η = efficiency

T_h = temperature high level (K)

T_c = temperature low level (K)

As a consequence, to attain maximum efficiency the T_c would have to be as cold as possible. For 100% efficiency the T_c would have to equal 0 K. This is practically impossible, so the efficiency is always less than 1 (less than 100%).

Change in entropy > 0,
irreversible process

Change in entropy = 0,
reversible process

Change in entropy < 0,
impossible process

Entropy is used to define the unavailable energy in a system. Entropy defines the relative ability of one system to act to an other. As things moves toward a lower energy level, where one is less able to act upon the surroundings, the entropy is said to increase.

- For the universe as a whole the entropy is increasing!

Entropy definition

Entropy is defined as :

$$S = H / T \quad (2)$$

where

$$S = \text{entropy (kJ/kg K)}$$

$$H = \text{enthalpy (kJ/kg)}$$

$$T = \text{absolute temperature (K)}$$

A change in the entropy of a system is caused by a change in its heat content, where the change of entropy is equal to the heat change divided by the average absolute temperature (T_a):

$$dS = dH / T_a \quad (3)$$

The sum of (H / T) values for each step in the Carnot cycle equals 0. This only happens because for every positive H there is a countering negative H , overall.

Carnot Heat Cycle

In a heat engine, a gas is reversibly heated and then cooled. A model of the cycle is as follows: State 1 --(isothermal expansion) --> State 2 --(adiabatic expansion) --> State 3 --(isothermal compression) --> State 4 --(adiabatic compression) --> State 1

State 1 to State 2: Isothermal Expansion

Isothermal expansion occurs at a high temperature T_h , $dT = 0$ and $dE_1 = 0$. Since $dE = H + w$, $w_1 = -H_1$. For ideal gases, dE is dependent on temperature only.

State 2 to State 3: Adiabatic Expansion

The gas is cooled from the high temperature, T_h , to the low temperature, T_c . $dE_2 = w_2$ and $H_2 = 0$ (adiabatic).

State 3 to State 4: Isothermal Compression

This is the reverse of the process between states 1 and 2. The gas is compressed at T_c . $dT = 0$ and $dE_3 = 0$. $w_3 = -H_3$

State 4 to State 1: Adiabatic Compression

This is the reverse of the process between states 2 and 3. $dE_4 = w_4$ and $H_4 = 0$ (adiabatic).

The processes in the Carnot cycle can be graphed as the pressure vs. the volume. The area enclosed in the curve is then the work for the Carnot cycle because $w = - \text{integral} (P dV)$. Since this is a cycle, dE overall equals 0. Therefore,

$$-w = H = H_1 + H_2 + H_3 + H_4$$

If you decrease T_c , then the quantity $-w$ gets larger in magnitude.

if $-w > 0$ then $H > 0$ and the system, the heat engine, does work on the surroundings.

The laws of thermodynamics were determined empirically (by experiment). They are generalizations of repeated scientific experiments. The second law is a generalization of experiments dealing with entropy--it is that the dS of the system plus the dS of the surroundings is equal to or greater than 0.

- Entropy is not conserved like energy!

Example - Entropy Heating Water

A process raises 1 kg of water from 0 to 100°C (273 to 373 K) under atmospheric conditions.

Specific enthalpy at 0°C (h_f) = 0 kJ/kg (from steam tables) (Specific - per unit mass)

Specific enthalpy of water at 100°C (h_f) = 419 kJ/kg (from steam tables)

Change in specific entropy:

$$\begin{aligned}dS &= dH / T_a \\&= (419 - 0) / ((273 + 373)/2) \\&= \underline{1.297} \text{ kJ/kgK}\end{aligned}$$

Example - Entropy Evaporation Water to Steam

A process changes 1 kg of water at 100°C (373 K) to saturated steam at 100°C (373 K) under atmospheric conditions.

Specific enthalpy of steam at 100°C (373 K) **before** evaporating = 0 kJ/kg (from steam tables)

Specific enthalpy of steam at 100°C (373 K) **after** evaporating = 2 258 kJ/kg (from steam tables)

Change in specific entropy:

$$\begin{aligned}dS &= dH / T_a \\&= (2\ 258 - 0) / ((373 + 373)/2) \\&= \underline{6.054} \text{ kJ/kgK}\end{aligned}$$

The total change in specific entropy from water at 0°C to saturated steam at 100°C is the sum of the change in specific entropy for the water, plus the change of specific entropy for the steam.

Example - Entropy Superheated Steam

A process superheats 1 kg of saturated steam at atmospheric pressure to 150°C (423 K).

Specific total enthalpy of steam at 100°C (373 K) = 2 675 kJ/kg (from steam tables)

Specific total enthalpy of superheated steam at 150°C (373 K) = 2 777 kJ/kg (from steam tables)

Change in specific entropy:

$$\begin{aligned}dS &= dH / T_a \\&= (2\ 777 - 2\ 675) / ((423 + 373)/2) \\&= \underline{0.256} \text{ kJ/kgK}\end{aligned}$$