



Entropy, Temperature, Free Energy, and Entropic Force

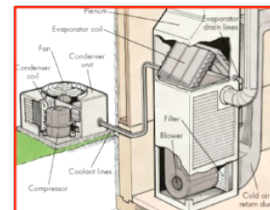
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Thermodynamics

- **Thermodynamics** is a physical science that studies the effects on material bodies, and on radiation in regions of space, of transfer of heat and of work done on or by the bodies or radiation. It interrelates macroscopic variables, such as temperature, volume, and pressure, which describe physical properties of material bodies.





Laws of Thermodynamics

- **The Zeroth Law:** If system *A* and system *B* are in thermal equilibrium with system *C*, then system *A* is in thermal equilibrium with system *B*
- **The First Law:** Increase in internal energy of a system = heat supplied to the system + work done on the system

The change in internal energy of a system is equal to the heat added to the system minus the work done by the system.

$$\Delta U = Q - W$$

Change in
internal
energy

Heat added
to the system

Work done
by the system



Laws of Thermodynamics

- **The Second Law:** When two isolated systems in separate, each in thermodynamic equilibrium in itself are allowed to interact, breaking the isolation that separates the two systems, allowing them to exchange matter or energy, they will eventually reach a mutual thermodynamic equilibrium. The sum of the entropies of the initial, isolated systems is less than or equal to the entropy of the final combination of exchanging systems. In the process of reaching a new thermodynamic equilibrium, total entropy has increased, or at least has not decreased.



Laws of Thermodynamics

- According to the second law of thermodynamics, in a reversible heat transfer, an element of heat transferred, δQ , is the product of the temperature (T), both of the system and of the source or destination of the heat, with the increment (dS) of the system's conjugate variable, its entropy (S):

$$\delta Q = T dS .$$

- **The Third Law:** The entropy of a perfect crystal at absolute zero is exactly equal to zero.



Entropy

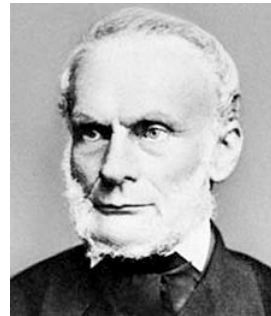
- **Entropy** is a thermodynamic property that can be used to determine the energy available for useful work in a thermodynamic process, such as in energy conversion devices, engines, or machines.





Entropy

- The term “Entropy” was first coined by Rudolf Clausius in 1865.
- It was originally from Greek εντροπία [entropía], *a turning toward*, from εν- [en-] (in) and τροπή [tropē] (turn, conversion).



Entropy – Thermodynamic

- The thermodynamic definition was developed in the early 1850s by Rudolf Clausius and essentially describes how to measure the entropy of an isolated system in thermodynamic equilibrium.
- Importantly, it makes no reference to the microscopic nature of matter.
- Thermodynamic **entropy** has the dimension of energy divided by temperature, and a **unit** of joules per kelvin (J/K) in the SI unit system.



Carnot Cycle - 1

- The **Carnot cycle** is a theoretical thermodynamic cycle proposed by Nicolas Léonard Sadi Carnot in 1824 and expanded by Benoit Paul Émile Clapeyron in the 1830s and 40s.
- It can be shown that it is the most efficient cycle for converting a given amount of thermal energy into work, or conversely, creating a temperature difference (e.g. refrigeration) by doing a given amount of work.

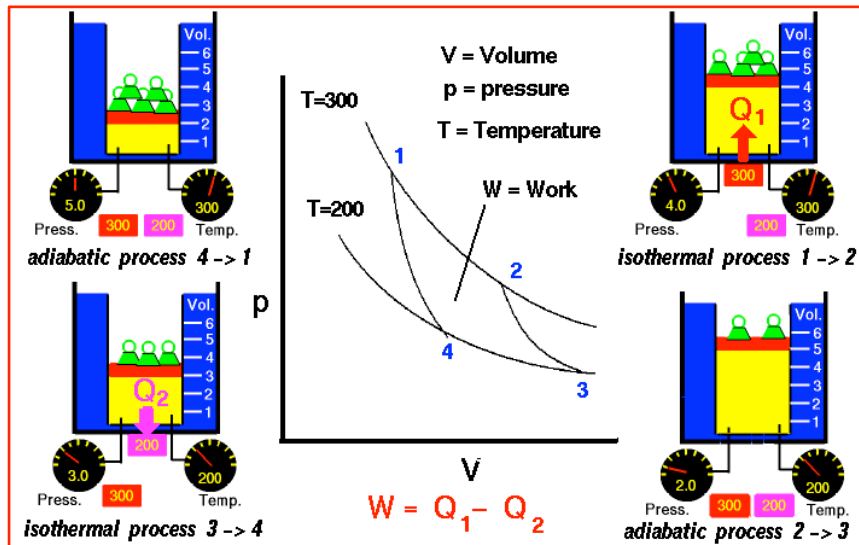


Carnot Cycle - 2

- Every thermodynamic system exists in a particular thermodynamic state. When a system is taken through a series of different states and finally returned to its initial state, a thermodynamic cycle is said to have occurred.
- In the process of going through this cycle, the system may perform work on its surroundings, thereby acting as a heat engine.
- Carnot heat engine is only a theoretical limit and cannot be built in practice.

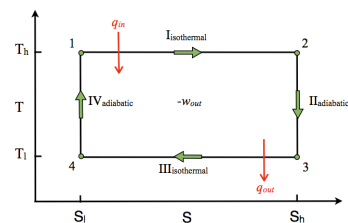


Carnot Cycle - 3



Carnot Cycle - 4

- 4 steps in the Carnot Cycle.
 - (1 to 2): Reversible isothermal expansion of the gas at the “hot” temperature, T_H (isothermal heat addition).
 - (2 to 3): Isentropic (reversible adiabatic) expansion of the gas (isentropic work output).
 - (3 to 4): Reversible isothermal compression of the gas at the “cold” temperature, T_C . (isothermal heat rejection).
 - (4 to 1): Isentropic compression of the gas (isentropic work input).





Carnot Cycle - 4

$$Q = \int_A^B T dS$$

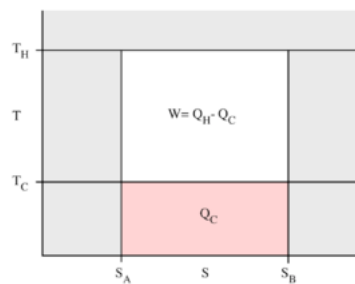
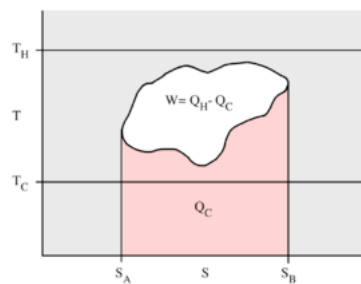
$$W = \oint PdV = \oint (dQ - dU) = \oint (TdS - dU)$$

$$W = \oint PdV = (T_H - T_C)(S_B - S_A)$$

$$Q_H = T_H(S_B - S_A)$$

$$Q_C = T_C(S_B - S_A)$$

$$\eta = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H}$$



Entropy – Statistical Mechanics

- The statistical definition was developed by Ludwig Boltzmann in the 1870s by analyzing the statistical behavior of the microscopic components of the system.
- Boltzmann showed that this definition of entropy was equivalent to the thermodynamic entropy to within a constant number which has since been known as Boltzmann's constant.





Entropy – Statistical Mechanics

- The interpretation of entropy in statistical mechanics is the measure of uncertainty, which remains about a system after its observable macroscopic properties, such as temperature, pressure and volume, have been taken into account.
- For a given set of macroscopic variables, the entropy measures the degree to which the probability of the system is spread out over different possible microstates.



Entropy – Statistical Mechanics

- Specifically, entropy is a logarithmic measure of the density of states:

$$S = -k_B \sum_i P_i \ln P_i,$$

- where k_B is the Boltzmann Constant, equal to $1.38065 \times 10^{-23} \text{ J K}^{-1}$. The summation is over all the possible microstates of the system, and P_i is the probability that the system is in the i th microstate.



Entropy – Statistical Mechanics

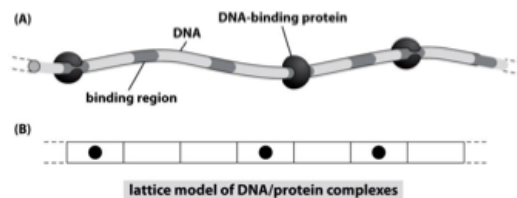
- In what has been called *the fundamental assumption of statistical thermodynamics*, the occupation of any microstate is assumed to be equally probable (i.e. $P_i = 1/\Omega$ since Ω is the number of microstates); this assumption is usually justified for an isolated system in equilibrium. Then the previous equation reduces to:

$$S = k_B \ln \Omega$$



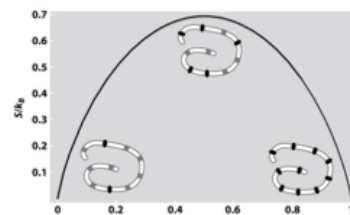
Entropy – Example

- Without considering mechanical force, electrostatic force etc., other than thermal fluctuation. Lac repressor protein on DNA-binding sites:



$$S = k_b \ln W(Np, N)$$

$$W(Np, N) = N! / Np!(N - Np)!$$





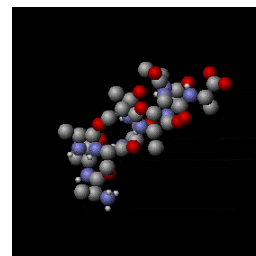
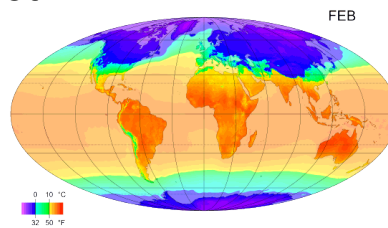
Entropy – Comparison

- The thermodynamic definition of entropy provides the experimental definition of entropy, while the statistical definition of entropy extends the concept, providing an explanation and a deeper understanding of its nature.



Temperature

- **Temperature** is a physical property of matter that quantitatively expresses the common notions of hot and cold. Objects of low temperature are cold, while various degrees of higher temperatures are referred to as warm or hot.





Temperature – Statistical Mechanics

- Statistical Mechanics provides a microscopic explanation of temperature, based on macroscopic systems' being composed of many particles, such as molecules and ions of various species, the particles of a species being all alike. It explains macroscopic phenomena in terms of the mechanics of the molecules and ions, and statistical assessments of their joint adventures.
- In the statistical thermodynamic approach, degrees of freedom are used instead of particles.



Free Energy

- In thermodynamics, the **Helmholtz free energy** is a thermodynamic potential that measures the “useful” work obtainable from a closed thermodynamic system at a constant temperature and volume. For such a system, the negative of the difference in the Helmholtz energy is equal to the maximum amount of work extractable from a thermodynamic process in which temperature and volume are held constant. Under these conditions, it is minimized at equilibrium.

$$A \equiv U - TS$$



Free Energy

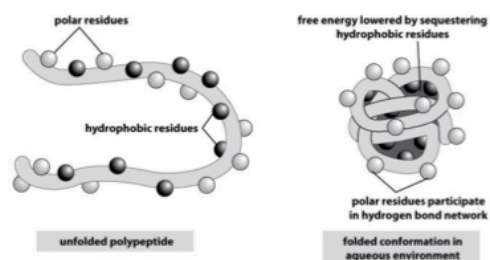
Free energy reflects the competition between energy and entropy

At lower temperature, energy dominates.

At higher temperature entropy dominates.

Contacts between amino acids can result in net energy lowering in the folded state. (energetically favorable)

The many different conformations available to the unfolded protein increases its entropy. (entropically favorable)



So higher temperature protein denatures and we get fried egg.



Entropic Force

- In physics, an **entropic force** acting in a system is a phenomenological force resulting from the entire system's statistical tendency to increase its entropy, rather than from a particular underlying microscopic force.

