

How to Find Order in Explaining a Disordered Physical Parameter?

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Abstract

The concept of entropy and the spontaneity of a process are the main contents that one encounters while studying the second law of thermodynamics. In this article, a variety of natural phenomena have been discussed which ultimately explains the concept behind the introduction of various physical statements. Also a different approach has been illustrated that may be introduced while explaining the concept of entropy to students.

Key words: entropy, spontaneous, disorder, thermodynamics

1. Introduction

Introducing the concept of entropy in a class of undergraduate students require an understanding of the necessity of why such a physical parameter is at all necessary to be framed. This article is a conglomeration of how the concept can be introduced in a class, relating natural phenomenon to be the cause behind such a formulation.

Entropy is associated with a large number of definitions which shall be explored under various sub headings¹. Initially I start with the basic assumption that few reactions occur spontaneously in the universe, unaided by any kind of external agitation. Such changes proceed spontaneously in one direction, but not in the other.

2. Direction & nature of spontaneous process

There are two basic types of spontaneous physical process:

(i) Matter tend to become dispersed: Dispersion of a dye solution in a saucer of clean pure water

The colour of dye spreads into uncoloured regions of water. Such a mixing continues until the composition in the saucer is homogeneous. We never see the reverse process with the dye suddenly concentrating into a coloured blob surrounded by clean, uncoloured water. The second law of thermodynamics speaks on the direction of the spontaneous process.

(ii) Energy tends to become dispersed: Equalizing the temperature when one end of bath is hot and the other end is cold

When the water at one end of bath tub is hot and cold at the other end, it has been found that temperature equilibration occurs after some time even without stirring. Molecules of hot and

cold water in a bath exchange energy in order to maximize the randomness of their energies. With no chemical reaction taking place, and no bond breaking or making taking place, the cause behind such a process is to increase disorder or randomness in the system. On plotting the number of molecules attaining energy E vs. energy of water molecule, we get a broad Gaussian distribution type of curve. Such energetic disorder is a consequence of having a broad range of energies.

Spilling a bowl of sugar: changes in the extent of disorder

It is easy to create a disorder but it is difficult to create order. A bowl of sugar, flour or salt dropped cause a mess, with the powder spreading everywhere and covering the maximum area possible. Spatial distribution of granules ensures a range of energies- some particles residing on higher surfaces than others creating a range of potential energies. Some granules travels faster than the other, ensuring a range of kinetic energies. It requires effort to clean sugar and reestablish order. Thus nature always seeks to maximize disorder and reversing a spontaneous process requires an input of energy.

3. Concept of Entropy

A room containing fresh oranges acquires their fragrance within a few hours / Sublimation of solid Iodine / Drying of damp cloths: This explains spontaneity and the sign of ΔS

Organic terpene (+) – limonene, present in oranges, is a non polar molecule which readily evaporates at room temperature to form vapour. Such evaporation takes place because gaseous limonene has a greater extent of energetic disorder, greater scope of physical movement and therefore greater entropy than liquid limonene. If the final disorder of a spontaneous process is greater than the initial disorder, then $\Delta S = S$ (final) – S (initial) is accompanied by a positive sign.

Other natural phenomenon that supports the direction of spontaneous process includes a slight purple hue on top of solid iodine contained in a bottle. This suggests the process of sublimation of solid iodine to vapour. This argument says nothing about the rate of sublimation, which is very slow at room temperature.

Damp cloths become dry when hung outside on a washing line even in the absence of a breeze. The liquid water molecules spontaneously leave the surface of the fabric in the form of gaseous water.

The change in entropy may be defined as $\Delta S = q_{rev} / T$: Qualitatively discuss the significance of the term “reversible”, why heat (and not work) appears in the numerator, and why temperature appears in the denominator.

The concept of reversibility refers to the ability of an infinitesimal change in a variable to change the direction of a process. Mechanical reversibility refers to the equality of pressure acting on either side of a movable wall. Thermal reversibility (as stated in the above equation) refers to equality of temperature on either side of a thermally conducting wall. Reversible transfer of heat is smooth, careful and restrained transfer between two bodies at the same temperature.

Work is the transfer of energy that achieves or utilizes uniform motion of some kind in the surroundings. For instance electrical work corresponds to electrons being pushed in the same direction through a circuit. Mechanical work corresponds to atoms being pushed in the same direction against an opposing force. On the other hand, heat is the mode of transfer of energy that achieves or utilizes random motion in the surroundings. For example, a fuel burning generates a random molecular motion in its vicinity. One should consider the change in entropy synonymous to a change in the degree of dispersal of energy and matter- which is proportional to the energy transfer that takes place by making use of random motion rather than orderly motion.

The presence of temperature in the denominator takes into account the extent of randomness of motion that is already present. If a given quantity of heat is transferred as heat to a hot object, then the additional randomness of motion generated is less significant than if the same quantity of heat is transferred as heat to a cold object in which the atoms have less thermal motion.

Entropy makes water run uphill in trees – Illustrating entropy of mixing and osmotic pressure
When pure water is in contact with cellular fluids (water with other substances dissolved in it), then water will mix with the fluid to dilute it. The driving force behind such mixing is entropy, and the diluted fluid is in a higher state of disorder than pure water. This kind of mixing takes place even in presence of a semi permeable membrane (osmosis). Other examples include that a carrot becoming limp through drying can be restored to turgidity (crispness) by immersion in water. Water passes through the membrane of the carrot to dilute its highly concentrated cellular fluids. The leaves of trees are continuously losing water to the atmosphere by the process of transpiration. There is an enhanced solute concentration in the fluid of the leaves that generates an osmotic pressure forcing ground water in the roots to travel through the trunk against gravity through a column as high as 364ft without the aid of a pump. The driving force behind such a phenomena is the osmotic pressure and the inherent tendency to increase the disorder state by entropy of mixing.²

Crystallization of a solute: This explains thermodynamic spontaneous process occur if and only if ΔS (total) [= ΔS (system) + Δ (surrounding)] is positive

The extent of solute disorder decreases during crystallization. But crystallization is a spontaneous process. To explain such a natural phenomenon, we need to include the change in disorder of both solute and solvent molecules before and after such a process. Before crystallization, each solute particle is bounded to few solvent molecules, and that limits the freedom of solvent molecules. During crystallization, since many such water molecules are released, there is a sizeable increase in the entropy of the solvent (ΔS surrounding is positive). Crystallization makes the solute molecules more ordered, and that decrease the entropy of solute (ΔS system is negative). The overall entropy change (ΔS total) is positive as ΔS surrounding $\gg \gg \Delta S$ system.

Dust particles move more quickly by Brownian motion in warm water: Explains entropy as a function of temperature

Dust particles, when viewed under a microscope, move randomly executing Brownian motion. Water molecules move continuously as a consequence of their own internal energy. Hundreds of such water molecules 'hold' on to the underside of each dust particle by surface tension. This is the cause for the Brownian movement of dust on water. Warming the water increases the internal energy and consequently its entropy. It causes the water to move faster than if the water was cool. Thus dust particles attached to water molecules are seen to undergo Brownian motion more rapidly on warming.

Jam of a Jam tart burns more than the pastry when heated in oven: proves the relationship between entropy and heat capacity

Even though both the pastry and the jam in a hot jam tart are at the same temperature, the jam burns the tongue more than the pastry. Assuming that sucrose is a major component in the jam tart, its specific heat capacity at constant pressure (C_p) is $425 \text{ JK}^{-1} \text{ mol}^{-1}$. It means we need to add 425J of energy to increase its temperature by 1K or in other words, the liquid jam stores more energy than when it is in pure solid state (heat capacity of a liquid is always greater than the heat capacity of the respective solid because liquid having a greater amount of energetic disorder has a greater entropy.). The jam, on cooling to the same temperature as the tongue gives out more energy; the tongue cannot absorb all, so the energy not absorbed burns the mouth.

A simple method for showing that entropy is a function of state

G. K. Vemulapalli³ in his article has tried to establish the above fact without exploiting the concept of the Carnot engine. Introducing entropy via the operation of a reversible heat engine is a cumbersome and time consuming process. He made a convincing proof that the entropy of the ideal gas is a function of state, $\oint dq_{rev}(i)/T = 0$, where $i = \text{ideal gas}$. However we all know that the thermodynamic relation that holds for an ideal gas may not be obeyed for any arbitrary substance. Djurdjevic and Gutman⁴ in their article has just extended the approach to prove that $\oint dq_{rev}(s)/T = 0$ where $s = \text{arbitrary substance}$.

Unfolding of lysozyme: Entropy change associated with a phase transition

Lysozyme is an enzyme that breaks down bacterial cell walls, unfolds at a transition temperature of 75.5°C and the standard enthalpy of transition is 509 kJ mol^{-1} along with the entropy of transition being $+1.46 \text{ kJ K}^{-1} \text{ mol}^{-1}$. At the molecular level, a positive entropy change is explained by the dispersal of matter and energy that accompanies on unfolding the compact three dimensional structure of protein in to a long flexible chain that can adopt many different conformations as it writhes about in solution.

Inequality of Clausius

The Clausius inequality may be explained in a simplistic way as discussed by D. A. McQuarrie and J. D. Simon.⁵ For an open system, dS for any spontaneous infinitesimal process = Entropy created by the irreversible process within the system (dS_{prod} , always

positive) + Entropy due to the energy as heat exchanged between the system and its surroundings (dS_{exch} , may be positive, negative or zero).

$dS = \delta q/T$ where $\delta q = \delta q_{\text{rev}}$ if the exchange is reversible and $\delta q = \delta q_{\text{irr}}$ if the exchange is irreversible.

$$dS = dS_{\text{prod}} + dS_{\text{exch}} = dS_{\text{prod}} + \frac{\delta q}{T}$$

For a reversible process, $dS_{\text{prod}} = 0$ & $dS_{\text{exch}} = \frac{\delta q_{\text{rev}}}{T}$

So $dS = \frac{\delta q_{\text{rev}}}{T}$ for reversible process, Eq [1]

For an irreversible or spontaneous process, $dS_{\text{prod}} > 0$ & $dS_{\text{exch}} = \frac{\delta q_{\text{irr}}}{T}$

So $dS > \frac{\delta q_{\text{irr}}}{T}$ for irreversible process Eq [2]

Thus combining Equation 1 & 2, $dS \geq \frac{\delta q}{T}$ where the equality sign holds for reversible process and the inequality sign holds for irreversible process.

Entropy change in mixing of ideal gases at constant T & p: a fallacy exists in few statements

We know that entropy change on mixing ideal gases follows the following equation:

$$n_A A [g, V_A, T] + n_B B [g, V_B, T] = n (A+B) [g, V = V_A + V_B, T]$$

$$\Delta S_{\text{mix}} = -nR [x_A \ln x_A + x_B \ln x_B]$$

Thus mixing of two (or more) different ideal gases is a process that causes an increase in disorder. This increase in disorder results in an increase in entropy. However, Arieh Ben-Naim⁶ have exemplified that increase in disorder cannot in general be associated with an increase in entropy. Also he cleared a fallacy that exists in the statement “Mixing of different ideal gases is an inherently spontaneous irreversible process”. He cited a process of demixing of ideal gases using semipermeable membrane which is a spontaneous irreversible process. Although they are rare, they do occur in nature. If one vigorously mixes water with oil and let it settle, the two liquids will demix spontaneously. Also it has been illustrated that it is the expansion of the gas rather than mixing that acts as a driving force for the expansion.

Thermodynamic Temperature Scale: concept developed from Clausius inequality

Lee Hong Yi⁷ has illustrated a new approach to deduce the Clausius inequality based on simple deduction. The entropy and the thermodynamic temperature scale follows naturally from the Clausius and Thomson statements of the second law of thermodynamics.

4. Conclusion

This paper has attempted to introduce the concept of entropy from various angles. The introduction simplifies when one takes help of common day to day processes to relate the cause behind such formulation. Spontaneous process, concept of entropy has been elaborately discussed, ending with the thermodynamic temperature scale statement.

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