

Entropy

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Part of a book on [Thermodynamics](#)

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Here enters the leading role—entropy.

What is entropy?

Why is it introduced?

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Entropy steals the show

Isolated systems let us formulate the [basic algorithm of thermodynamics](#). The algorithm mentions no entropy. How does entropy enter the play of thermodynamics?

An isolated system flips among a set of quantum states. Denote the number of quantum states by Ω . Define the entropy of the isolated system by

$$S = \log \Omega$$

By definition, entropy of an isolated system stands for the phrase “the logarithm of the number of quantum states”.

We will soon explain why we hide Ω behind a log. The number of quantum states of an isolated system contains physics. Logarithm eases algebra, but adds no physics. It is the algebraic convenience that lets entropy steal the show from the number of quantum states.

Twitter [Entropy steals the show](#)

Do not explain entropy in terms of disorder

The above definition answers the question, “What is entropy?” In explaining entropy, many books use the word “disorder”. The word explains nothing. Entropy is a well-defined, measurable property. It needs no help from an undefined, nebulous notion like “disorder”. Delete all sentences that contain the word “disorder”, and you miss nothing.

People also use the word entropy to mean disorder. “This committee is full of entropy, but has no energy!” Such usage colors conversations, but does not enhance communication. Entropy is a precise and measurable quantity. Disorder is neither.

Let us remove all embellishments and focus on what entropy is: the logarithm of the number of quantum states of an isolated system. No more, no less.

2019 Styer Entropy as Disorder: History of a Misconception [Tweet](#)

Entropy is extensive

Why do we hide the number of quantum states Ω behind a log?

Two separately isolated systems. Consider two isolated systems, A and B. Isolated system A has one sample space of Ω_A quantum states, labeled as

$$\{a_1, a_2, \dots, a_{\Omega_A}\}.$$

Isolated system B has another sample space of Ω_B quantum states, labeled as

$$\{b_1, b_2, \dots, b_{\Omega_B}\}.$$

The two systems are *separately isolated*. Together they constitute a *composite*, which is also an isolated system. Each quantum state of this composite is specified by a quantum state of one isolated system, a_i , and a quantum state of the other isolated system, b_j . All such combinations together constitute the sample space of the composite. The total number of all such combinations is the product:

$$\Omega_{\text{composite}} = \Omega_A \Omega_B.$$

Turn a product to a sum. Recall a property of logarithm:

$$\log (\Omega_A \Omega_B) = \log \Omega_A + \log \Omega_B.$$

Thus, the entropy of a composite of two separately isolated systems is the sum of the entropies of the two individual isolated systems.

We now see the significance of logarithm: the function turns a product into a sum. The entropy of a system is the sum of the entropies of its parts, each part being separately isolated. Such an additive quantity is *extensive*. Thus, entropy is extensive, but the number of quantum states is not.

Logarithm of any base will do. For convenience, we will use the natural base e . The number e simplifies the derivative of logarithm. Recall a fact of calculus for logarithm of natural base:

$$d \log x / dx = 1/x$$

For any other base b , recall that

$$\log_b x = (\log_b e)(\log_e x), \text{ so that}$$

$$d \log_b x = (\log_b e)/x$$

The prefactor clutters the formula and serves no purpose.

For example, the entropy for a hydrogen atom isolated at the second energy level is

$$\log 8 = 2.079$$

The value of entropy is a pure number. Incidentally, I found this value by entering “ln 8” in the google search box.

Exercise. In defining entropy, we need a function that obeys $f(xy) = f(x) + f(y)$. Show that the logarithm is the only candidate.

Exercise. Given four types of ice cream (vanilla, strawberry, chocolate, pistachio) and three types of toppings (sprinkles, caramel, oreos), how many pairs of ice cream and topping can you make? List all pairs.

Entropy is absolute

By definition, the entropy of an isolated system = \log (the number of quantum states of the isolated system), $S = \log \Omega$.

Zero entropy is not something arbitrary, but has empirical significance. Zero entropy corresponds to an isolated system of a single quantum state. Like volume, entropy is absolute.

Needless reference state. Many tables list entropies of a pure substance at various states relative to the entropy of the substance at a particular state, called the reference state.

This practice has no merit. Some applications involve the change of entropy from one state to another, but other applications require absolute entropy. Indeed, we would be baffled if relative volumes were tabulated instead of absolute volumes. Why should we tolerate relative entropies?

Nobel lecture. Nernst, [Studies in chemical thermodynamics](#), 1921.

Entropy is dimensionless, but is given fake units

By definition, $S = \log \Omega$, entropy is *dimensionless*.

Fake unit, J/K. By a historical accident, however, entropy is given a unit, Joule/Kelvin, J/K. Write

$$S = k_B \log \Omega$$

Here k_B is called the Boltzmann constant. In 2019, an international committee named an exact value for this constant:

$$k_B = 1.380649 \times 10^{-23} \text{ J/K}$$

In practical calculations, take $k_B = 1.38 \times 10^{-23} \text{ J/K}$.

Wikipedia [The 2019 redefinition of the SI base units](#)

Caution. The unit J/K is a fake unit, and the Boltzmann constant contains no physics, so you do not need to learn anything about it beyond the value set by the committee. But if you are curious how we get ourselves into this situation, read on.

As we note [elsewhere](#), the Boltzmann constant is the conversion factor between two units of temperature, Joule and Kelvin:

$$1 \text{ Kelvin} = 1.380649 \times 10^{-23} \text{ Joule}$$

The Boltzmann constant does no honor to the three great scientists who helped to create the play: Joule, Kelvin, Boltzmann. The Boltzmann constant is just as mundane as any other conversion of units:

$$1 \text{ inch} = 2.54 \text{ cm}$$

The Boltzmann constant k_B clutters equations.

Worse, the fake unit, Joule/Kelvin, gives an impression that the concept of entropy depends on the concepts of energy and temperature. This impression is wrong. As we have seen, entropy and energy are distinct properties. As we will see, [temperature is the child of the union of entropy and energy](#).

Exercise. Wiki [Boltzmann constant](#). Describe the history of the fake unit for entropy, J/K.

Fake unit, kJ/kmol-K. One fake unit breeds another. Entropy is an extensive property, and is often reported by entropy per mole. [The 2019 redefinition of the SI base units](#) defines a mole as

$$1 \text{ mole} = 6.02214076 \times 10^{23} \text{ items}$$

This conversion factor is called the Avogadro constant, N_A . In practical calculations, take $N_A = 6.022 \times 10^{23} \text{ items/mol}$.

Thus, entropy is often reported in the fake unit of kJ/kmol-K. To convert a value of entropy in the fake unit to dimensionless entropy per molecule, divide the value of entropy in the fake unit by the conversion factor

$$N_A k_B = 8.314 \text{ kJ/kmol-K}$$

This number is merely a conversion factor between units, and has nothing to do with gas. By another historical accident, the number is called the *universal gas constant*, R .

To convert a value of entropy in the fake unit kJ/kmol-K to dimensionless entropy per molecule, divide the value of entropy in the fake unit by the universal gas constant $R = 8.314 \text{ kJ/kmol-K}$. The previous sentence contains multiple myths and zero physics.

Fake unit, kJ/kg-K. The fake unit breeds yet another fake unit. Entropy is an extensive property, and is often reported by entropy per unit mass. For example,

$$1 \text{ kmol of H}_2\text{O molecules} = 18 \text{ kg}$$

This value is called molar mass of H_2O , and is given the symbol M . Thus, entropy is often reported in the fake unit of kJ/kg-K. To convert a value of entropy in the fake unit to dimensionless entropy per molecule, multiply the value of entropy in the fake unit by the conversion factor M/N_A .

Twitter [Entropy is dimensionless, but is given fake units](#)

Absolute entropy of water at 25 Celsius and 100 kPa

Busywork. The great play offers a clean definition, $S = \log \Omega$, but then some international committees thrust upon us a fake unit and a needless reference. They are blemishes of the great play. They cause busywork. May the busywork annoy you, but not harm you. To make sure that you are annoyed, I write these sections.

A large number of H_2O molecules constitute a pure substance. The molecules form a liquid at 25 Celsius and 100 kPa. In this state, water has an absolute entropy of

69.95 kJ/kmol-K

I found this value [online](#).

Recall the molar mass:

1 kmol of H_2O molecules = 18 kg

In the unit kJ/kg K, the absolute entropy of water at 25 Celsius and 100 kPa takes the value

$(69.95 \text{ kJ/kmol-K}) / (18 \text{ kg/kmol}) = 3.886 \text{ kJ/kg-K}$

The dimensionless entropy per molecule is

$(69.95 \text{ kJ/kmol-K}) / (8.314 \text{ kJ/kmol-K}) = 8.414$

This value is the absolute, dimensionless entropy per molecule in water at 25 Celsius and 100 kPa.

Wikipedia [Standard molar entropy](#) For a pure substance, absolute entropy at the standard state (25 Celsius and 100 kPa), in units of J/mol K, is called *absolute molar entropy*. Values for numerous pure substances have been tabulated. Here is an [example](#).

Absolute entropy of H_2O in various thermodynamic states

The [NIST steam table](#) sets the entropy to be zero for water at three-phase equilibrium. By convention, most steam tables set the entropy at this state to be zero, and list entropies in other states relative to this reference.

The same table lists entropy for water at 25 Celsius and 100 kPa:

0.36722 kJ/kg K

In the previous section, we have obtained the absolute entropy for water at 25 Celsius and 100 kPa:

3.886 kJ/kg K

For water at 25 Celsius and 100 kPa, the absolute entropy and the relative entropy differ by

$3.886 \text{ kJ/kg-K} - 0.36722 \text{ kJ/kg-K} = 3.519 \text{ kJ/kg-K}$

Thus, the absolute entropy of water at three-phase equilibrium is

3.519 kJ/kg K

To convert the relative entropies in the steam tables to absolute entropies, simply add 3.519 kJ/kg-K to every entry.

For example, I list the absolute entropies of ice, water, and steam in three-phase equilibrium.

	relative entropy kJ/(kg-K)	absolute entropy kJ/(kg-K)	absolute dimensionless entropy per molecule	Number of quantum states Ω per molecule
ice	- 1.221	2.298	4.976	144.89
water	0	3.519	7.619	2036.52
steam	9.156	12.68	27.44	8×10^{11}

Note the procedures of conversion:

- (absolute entropy at state A) = (relative entropy at state A) + (absolute entropy of the state of water at the three-phase equilibrium).
- (entropy in kJ/kg-K) = (dimensionless entropy)(specific gas constant).
- The specific gas constant for H₂O is $R/M = (8.314 \text{ kJ/kmol-K})/(18 \text{ kg/mol}) = 0.46 \text{ kJ/kg-K}$.

Exercise. 1 kg of H₂O molecules are in a state of three-phase equilibrium, with 0.5 kg of ice, 0.4 kg of water, and 0.1 kg of steam. What is the entropy in this state? What is the volume of this state?

Exercise. Calculate the number of quantum states per CO₂ molecule in each phase at the three-phase equilibrium. List the references where you find the data needed for the calculation.

Number of quantum states per molecule

The following two functions are inverse to each other:

$$y = \log x$$

$$x = \exp y$$

Recall the definition of absolute, dimensionless entropy, $S = \log \Omega$. Given the absolute, dimensionless entropy per molecule in a state of a substance, the number of quantum states per molecule is

$$\Omega = \exp(S)$$

For water at 25 Celsius and 100 kPa, the absolute, dimensionless entropy per molecule is 8.414, so that the number of quantum states per molecule is

$$\Omega = \exp(8.414) = 4509.76$$

I do not have any intuition about this number of quantum states per molecule for water at 25 Celsius and 100 kPa. But let me develop some intuition by comparing this number with numbers of quantum states at other thermodynamic states of H_2O .

I list the numbers of quantum states per molecule in the thermodynamic states of ice, water, and steam in three-phase equilibrium.

In the state of ice, the molecules form a lattice and can not freely translate and rotate, giving a small number of quantum states.

In the state of water, the molecules can translate and rotate, but still touch one another, giving a larger number of quantum states.

In the state of steam, the molecules can fly, giving the largest number of quantum states: almost a trillion quantum states per molecule.

At 25 Celsius and 100 kPa, water has 4509.76 quantum states per molecule. In the three-phase equilibrium, water has 2036.52 quantum states per molecule. The change in the number of quantum states is modest when a substance changes thermodynamic state within the same phase.

Twitter [Number of quantum states per molecule](#)

Exercise. When water evaporates at 100 Celsius, how much does the evaporation amplify the number of quantum states per molecule?

Exercise. Graphite is a form of carbon. At 25 Celsius and 100 kPa, the absolute entropy of graphite is 5.740 kJ/K-kmol. How many quantum states per carbon atom are in the graphite?

Exercise. Carbon atoms can also aggregate in other forms, such as diamond, graphene, nanotube, and buckyball. Learn about these forms online, and find the entropy per carbon atom in each form.

Subset entropy

Consider an isolated system with an internal variable. When the internal variable is free to change, the isolated system flips among a set of quantum states, called the sample space of the isolated system.

When the internal variable is fixed at a value x , the isolated system flips among quantum states in a subset of the sample space. Let $\Omega(x)$ be the number of quantum states in this subset.

Denote

$$S(x) = \log \Omega(x)$$

The function $S(x)$ stands for “the logarithm of the number of quantum states in the subset of the sample space of an isolated system when an internal variable is fixed at a value x ”.

For brevity, I call the function $S(x)$ the *subset entropy*.

Twitter [Subset entropy](#)

Basic algorithm of thermodynamics

We have [previously](#) stated the basic algorithm of thermodynamics in terms of $\Omega(x)$. Now we have defined $S(x) = \log \Omega(x)$. Because logarithm is an increasing function, increasing $\Omega(x)$ is equivalent to increasing $S(x)$. We now paraphrase the basic algorithm of thermodynamics in terms of the subset entropy $S(x)$.

1. Construct an isolated system with an internal variable x .
2. Find the subset entropy of the isolated system as a function of the internal variable, $S(x)$.
3. After the system is isolated and the internal variable is free to change, both for a long time, the system equilibrates at a value of x that maximizes $S(x)$.
4. Let $x = a$ and $x = b$ be two states of constrained equilibrium. A *process* from a to b is *impossible* if $S(a) > S(b)$, *reversible* if $S(a) = S(b)$, and *irreversible* if $S(a) < S(b)$.

How to “find” the subset entropy $S(x)$? This function is usually measured experimentally. We will give examples in later chapters, starting with the next chapter, “[thermal system](#).”

The basic algorithm of thermodynamics is hard to grasp in one go. No worries. The rest of the play runs the algorithm on numerous phenomena. Indeed, everything thermodynamic originates from this single algorithm. So long as you stay in touch with nature, you will have a lifetime to learn the algorithm.

Twitter [Basic Algorithm of Thermodynamics](#)

Entropy generation is a measure of irreversibility

Reversible processes are idealizations, and do not happen in nature. All actual processes are irreversible.

For an isolated system undergoing a process from one state of constrained equilibrium $x = a$ to another $x = b$, the difference, $S(b) - S(a)$, is a positive and dimensionless number, called the *entropy generation*, which measures the degree of irreversibility of the process. The entropy generation, $S(b) - S(a)$, depends on the two states of constrained equilibrium, a and b , but not on intermediate changes. Entropy generation is nature's currency for irreversibility.

An isolated system may have multiple internal variables. The basic algorithm of thermodynamics works just the same.

YouTube [Popular science video on entropy](#)

The second law of thermodynamics

The basic algorithm of thermodynamics dates back to Gibbs (1873), Clausius (1850), and Carnot (1824). The algorithm has many names, including the principle of the increase of entropy, second law of thermodynamics, free-energy minimization, availability analysis, exergy analysis, and entropy-generation analysis.

Not all statements of the second law are equivalent. Some are content-free, misleading, or wrong. We will list some historical statements of the second law of thermodynamics. They may sound like ancient philosophical pronouncements. They sound mysterious not because they are more profound than the basic algorithm of thermodynamics, but because they miss facts of nature (e.g., the rapid and ceaseless flips among quantum states, the fundamental postulate, the internal variables).

Here is one such statement made by Clausius (1865), in the same paper in which he coined the word entropy:

The entropy of the universe tends to a maximum.

Take the word “universe” to mean “an isolated system”. The statement is elegant but wrong, if taken literally. The entropy of an isolated system is $S = \log \Omega$, where Ω is the number of quantum states in the sample space of the isolated system. The entropy of an isolated system is a fixed number, not a function that can change value and be maximized.

To maximize something requires a function. To specify a function requires both a dependent variable, and one or many independent variables. In thermodynamics, the dependent variable is the subset entropy. The independent variable is the internal variable, which specifies the subset. When the internal variable is fixed at a value x , the isolated system flips among quantum states in a subset of the sample space. The number of quantum states in this subset is $\Omega(x)$, and the entropy of this subset is $S(x) = \log \Omega(x)$. When the internal variable can change values. It is the subset entropy $S(x)$ that tends to a maximum.

When elegance and clarity conflict, we go for clarity.

This book does not teach the history of thermodynamics. We do not attempt to read the mind of Clausius and decipher old pronouncements. Rather, we use the algorithm to direct calculation and measurement. In particular, the algorithm will let us count, experimentally, the number of quantum states in the subset of the sample space of an isolated system, $\Omega(x)$.

Twitter [What's wrong with Clausius's pronouncement?](#)