# What I Learned About Basic Thermodynamics

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**Abstract**

*Prior to very recently, I had several misconceptions about temperature and its relationship to energy. I could not very well explain why temperature had different units than heat, and although I had some intuitive sense of it, my intuitive sense was completely incorrect. Specifically, my previous understanding was that temperature was defined in such a way that it increased with energy and represented a store of energy. While this is an approximation of the truth, it is more a description of a common situation that follows from the definition of temperature, not a definition of temperature itself. I have now learned the proper definition of temperature, which I will explain here, along with the closely related concepts of entropy and enthalpy.*

## I. INTRODUCTION

When my friend Charlotte asked me to help her understand *enthalpy* ($H$), *entropy* ($S$), and *Gibbs free energy* ($G$), I was very confident. I had, after all, gotten a score of 720 on my Chemistry SAT II in high school, and furthermore had received a pass in the extremely intense pre-med version of Organic Chemistry at Cornell University, which I had taken simply because it was hard. I clearly knew this stuff at some point, even if I was having a hard time remembering it now.

Searching the Internet, however, it took me a long time to find any coherent definition of the terms in question. Specifically, I had quickly learned that this was the equation for Gibbs free energy:

$G = H - TS$

That is to say, the Gibbs free energy is calculated based on the enthalpy and entropy – and, randomly enough, temperature ($T$). This led to a very important question: What do entropy and enthalpy have to do with each other? How are they connected?

Unfortunately, I saw many Quora answers and Stack Overflow posts that to the contrary implied that they were completely different and unrelated – and any confusion between them, apparently, was explained by their similar-sounding names. If that were true – if they were completely unrelated – you would not expect to see them in the same equation. And why on earth was entropy being multiplied by temperature?

I had some understanding of this. Of the enthalpy, some of it was taken up by entropy/temperature in some way, and therefore wasn't "free" or useful for producing work. But that still didn't explain the exact nature of the $TS$ term.

Eventually, I figured out what was going on with entropy, and learned a lot more about a topic I thought I had very thoroughly understood. The result of my reading and attempts at comprehending is presented below.

Before we continue, I'd like to politely remind the reader that I'm talking about temperature in absolute terms, where 0 is absolute zero, the temperature colder than all possible temperatures, rather than the "zero degrees" we might talk about from time to time. For this paper, I'm also using metric units, because the resources on the Internet do not line up with the units my ancestors favored.

# II. Energy Dynamics: The First Law

## i. Enthalpy and Internal Energy

*Enthalpy* ($H$) is a measure of the *internal energy* ($U$) of a system[1], plus the amount of energy embodied in the system taking up space, which is $pV$ or pressure times volume, the amount of energy involved in the system not collapsing.

*Energy* ($E$) is a fundamental physical concept. The amount of energy in the entire universe is constant[2], but it can take many differnet forms. If the energy of one body[3] or system increases, some other system must have lost energy. Matter is really a form of energy, and mass and energy are convertable in Einstein's famous equation $E = mc^2$.

Conservation of energy is also the *First Law of Thermodynamics*, in addition to being a law in Newtonian Mechanics and other areas of physics[4].

*Internal energy* ($U$) includes many forms of energy: the chemical bonds of a system, the mass-energy of its constituent atoms, the kinetic energy of particles moving about *within* the system[5].

In fact, it is easier to list what forms of energy are not "internal": kinetic energy of the entire system (as opposed to things moving within it) and potential energy of the entire system in the context of an external field (as opposed to potential energy from interactions in internal fields), and, of course, the energy involved in taking up space ($pV$), although this is included in enthalpy:

$H = U + pV$

Note that the total energy of a system includes all the mass energy of all the particles in it, and is therefore too huge to care about. Generally, in chemistry, only changes in enthalpy are relevant, as opposed to total enthalpy.

## ii. Heat and Work

Before, we mentioned energy transfers. There are two types of energy transfer, *work* ($W$) and *heat* ($Q$). The convention is that heat is positive when it comes into the system, but work is positive when it is leaving the system, yielding the following equation:

$\Delta U = Q - W$

In situations where pressure and volume are not also changing, this is also a valid formula for $\Delta H$, as you can see from the equations above.

Heat is the automatic flow of energy from a *hotter* object to a *cooler* object – we shall discuss in a later section what it means for objects to be hotter and cooler, and why this flow is automatic. It is microscopic. Work is anything else, including moving physical objects a certain distance. Work is generally macroscopic. Both can be measured in units of energy.

As you can see, the amount of total heat that's been added to something directly effects the *enthalpy* – the *enthalpy* is increased by the sum of the total heat. As I said before, however, in spite of this, enthalpy is distinct from *temperature*.

# III. Entropy and the Second Law

## i. Entropy or Information, a Statistical Definition

Let's say we have 100 molecules in a very limited state. They are not moving at all, in a near-perfect crystal[6]. We can know exactly everything about these molecules from looking at this crystal except one thing: Which way are

[1] Future research: What counts as a system, exactly? Does it all have to be the same temperature? Clearly it has to be spatially continuous.

[2] Apparently some cosmological models allow for an influx of *dark energy* to explain why the universe's expansion is accelerating, but that is not relevant to the scale we're talking about.

[3] Definition, anybody?

[4] This leaves me unsure of how they work out the jurisdictional issue of which police forces will arrest you in case of violations.

[5] This is what I thought temperature was, but as we'll see later, temperature only correlates with this, and only in common situations.

[6] Spoiler: It's also at absolute zero temperature

they oriented? They can either be oriented one way or the other, and they have such a small dipole moment that it is essentially random[7].

The amount of information or *entropy* stored in this crystal is based on how many states there are. In this case, each molecule can be in one of two equally-likely positions, and so there are $2^{100}$ possible combinations.

The number of possible states can be used to give a value for entropy using Boltzmann's constant, and this formula inscribed on Ludwig Boltzmann's tombstone:

$S = k \ln W$

$k = 1.38064852 * 10^{23} \frac{J}{K}$

$S = 9.56992628 * 10^{-22} \frac{J}{K}$

This is an extremely small amount of entropy. This also means that one bit has a physical entropy of approximately $9.5699262 * 10^{-24}$, which is very small. In real life, bits are stored somewhat inefficiently in mechanisms that embody more entropy than that.

Why is there a natural logarithm? Well, this way, entropy increases linearly as the number of carbon monoxide molecules increases. Each additional molecule multiplies the number of *microstates* by 2, but increases the entropy by a constant amount. This is similar to how each bit doubles the amount of possible values, but increases the information by 1.

## ii. The Second Law: The Inexorable Passage of Time

Most physical laws are neutral as to time[8]. They work equally well forwards and backwards in time. Entropy is an exception. Total entropy increases with time. This is as fundamental a principle of the universe as the conservation of energy, and it defines *future* and *past*. Increases of entropy happen spontaneously. Decreases do not happen spontaneously – for them to happen at all, an even greater increase must happen elsewhere.

As it is written:

Humpty Dumpty sat on the wall
Humpty Dumpty had a great fall
All the king's horses and all the king's men
Couldn't put Humpty Dumpty back together again

*What does this mean?*[9] That the universe is structured thus, that the amount of disorder in it, whether the brokenness of eggs or the spiltness of milk, increases, and can only be decreased with great effort and even more disorder elsewhere, and that this cannot be escaped by either commoners or the leaders of our society. This is most certainly true[10].

This law is so universal that it inspired Stephen Hawking to seek an explanation for the one apparent loophole he saw: In a black hole, where was the information going? He developed the theory of Hawking radiation in response.

## iii. What is temperature?

As noted before, counterintuitively, temperature is not the sum of how much heat is in a system. Heat is used to describe energy moving because of differences in temperature. Specifically, temperature is defined based on the movements of heat: a body is *hotter* than a *cooler* body if heat spontaneously moves from the hotter one to the cooler one.

This is all well and good, but does not tell us how to assign a continuous number to temperature, only an ordering. Why can we say one temperature difference is twice as big as another? It's not because more heat transfers between them – our experience shows us that the rate at which heat moves is independent of the magnitude of the temperature difference. This definition only tells us which direction

[7] Spoiler: It's carbon monoxide, okay?

[8] You might think gravity is not neutral in that things fall down but not up. But things start out at rest at a high place and end up moving down at a certain speed. If they started out moving up at the same speed, they'd stop at that high place. That is the true time reversal. The reason this might not happen is because things break instead of bouncing and lose energy to friction; those, however, are both entropy-based processes.

[9] Channelling Martin Luther's writing style is not blasphemy, I don't think.

[10] Okay, that might be blasphemous.

heat flows.

Temperature is, for most people, defined practically: What number is shown on a thermometer? The scaling of temperature is defined by whatever makes mercury expand an equal amount. And not only does heat move on the basis of temperature, but adding heat to something will generally increase temperature. It certainly will not decrease it, and only in some situations – like that of a bucket of ice water – will it not increase it. In that way, temperature is a more measurable proxy for enthalpy.

Most heat is *sensible* heat. That means, when it flows into a body, it increases the measurable temperature – that is, you can *sense* it with a thermometer. In the case of a bucket of ice water, as heat flows in, the enthalpy is clearly increasing – energy is still conserved. The temperature doesn't start increasing until all the ice is melted. That makes it *insensible* heat. The fact that most heat in practical situations is sensible heat and that temperature is easier to measure than enthalpy makes temperature a good way of measuring certain forms of internal energy, even if not 100% accurate.

## iv. What has temperature got to do with entropy?

The formula that defines temperature as a number, however, is inextricably tied up with entropy:

$\delta S = \frac{\delta Q}{T}$

This relates entropy to incoming heat and temperature. As heat comes in, entropy always increases – unless the temperature is infinite or negative – and as heat goes out, entropy always decreases, with the same caveat.

The way this is framed in its standard formulation makes it look like a definition for entropy. Given that temperature is so much easier to measure, it makes sense from a historical perspective that entropy is the thing you'd need to make effort calculating or defining. However, we already have a definition of entropy, and a definition of energy[11], so this is more useful for our more theoretical purposes as a definiton of temperature[12]:

$T = \frac{\delta Q}{\delta S}$

Temperature is the trade-off rate between added energy and added entropy. When temperature is high, a lot of energy only adds a little entropy. When temperature is low, a lot of energy adds a lot of entropy.

This makes intuitive sense. As we add energy, entropy generally increases. The perfect crystal that only has entropy based on which ways the molecules are facing, now also has entropy based on how much these more energetic molecules are vibrating, and which molecules have busted out of their perfect formation, and on what axes they are vibrating[13].

But as we add more and more energy, the increase in entropy is smaller. Once we already have a gas, adding more energy just makes a few of the molecules move around faster – most are already moving as fast as they can.

This is the picture I have in my head, but not necessarily rigorous. What is intuitive, however, is that adding energy to create entropy would have diminishing returns.

## v. The Curious Case of the Ice-Water

Why, then, does temperature not increase in the case of ice water? You might think it's because the entropy is not increasing, but that would be a misinterpretation of the formula. When temperature is higher, that means energy will have less of an effect on entropy. When ice water is melting, each additional unit of energy freezes an equal amount of ice, adding an equal amount of entropy.

Once all the water is melted, additional energy is again less and less useful at creating new entropy, but while it's melting, each bit of ice provides an equal opportunity for new energy. This is why temperatures stay constant

[11] Though the full definition or even an attempt at a definition of energy is outside of the scope of this article.

[12] My father taught me how to rearrange equations like this, a long long time ago when I was a child.

[13] These are all examples that I just pulled out of my ass and may or may not represent what variables are actually relevant to calculating energy of slightly warmer crystals

for added heat during phase changes – they are entropy explosions.

## vi. Why is temperature the same as hotness?

We now have two distinct definitions: A body is *hotter* when heat flows out of it towards a *cooler* body, and a body's *temperature* is determined by how incoming heat affects entropy. So far, we have not established what everyone knows intuitively – that hotter bodies generally have higher temperature, and higher-temperature bodies generally have hotness.

The direction of heat flow is time dependent – heat flows in the direction of hotter to cooler, so that the cooler body warms up *over time*. Specifically, if you run time backwards, it goes the other direction. This should be some hint that entropy is involved in hotness.

The universe is trying to maximize its entropy. When a body has higher temperature, it means that energy gets less bang for its buck when creating entropy. This means that the same energy can provide more entropy in a lower-temperature body. Let's call the higher-temperature body $a$ and the lower-temperature body $b$, and assume a heat transfer of $Q$ so small that the temperature change is negligible[14]:

$$\Delta S_a = -\frac{Q}{T_a}$$

$$\Delta S_b = \frac{Q}{T_b}$$

$$\Delta S = \frac{Q}{T_b} - \frac{Q}{T_a}$$

Since $T_a$ is greater than $T_b$, the entropy change is greater in $b$ than in $a$, and therefore, the resulting total entropy of the entire system increases.

Since the entropy increases, this interaction will happen spontaneously. The energy is going where it does more to increase entropy – the cooler body.

[14]Go ahead and work it out with a temperature change, but then you'll have to use actual calculus rather than this pseudo-infinitessimal.

## vii. Negative Temperature

What does it mean for temperature to be negative? In the case of a negative temperature, more energy makes for less entropy. That follows from our definition of temperature.

A negative temperature item is very hot. If more energy makes for less entropy, it will want to get rid of all its energy, so that its entropy can increase. Any positive-temperature body will be better at turning energy into entropy than one that does so at a negative rate!

Therefore, this is an exception to the rule that higher temperatures mean things are hotter. The correspondence discussed in the previous section is not absolute.

Now, why would more energy decrease entropy? Let's say there's two states for a bunch of atoms: a high-energy state and a low-energy state. If they're all in the low-energy state, there is no entropy, as there's only one possible combination. If one goes to the high-energy state, we don't know which one it will be, so there's a lot of possible microstates and therefore more entropy.

The more are in a high state, the higher the temperature and the more entropy we have. Each additional atom switched does less to increase the number of possibilities, but still increases it – for a time.

But let's go from the other direction. If all of them are in a high-energy state, there is no entropy. But any switch from one of them from a high-energy state to a low-energy state will generate entropy. By losing energy, it would get more possible state arrangements and therefore more entropy! The situation where they're all high-energy state has negative temperature.

The switch-over is when half of them are in a high-energy state and half are in a low-energy state, a situation that has infinite temperature.

And yes, negative temperature things can exist in real life. They are apparently useful in lasers. I would avoid touching them and really burning your finger. They are hotter than something with infinite temperature. Good thing that the magnitude of temperature difference doesn't necessarily determine the rate of heat transfer!