

4.1: Introduction to Entropy

There are several ways to describe entropy. For example, word on the street is that entropy is the amount of randomness of a system. True, but let's add some nuances- entropy is randomness of a system *as created by heat*. Here is another description- the entropy of a material affects how heat changes it, like how the solubility of a salt in water dictates the solution's salinity. These descriptions are consistent with a change of entropy loosely defined as $\partial S = \frac{\partial q}{T}$, or $\Delta S = \frac{\Delta q}{T}$ if integrated. Let's apply this to situations that create "randomness" at a constant temperature such as a phase change. In this regard, it should be obvious that boiling water generates more entropy than melting ice. Consequently, if $\Delta S = \frac{\Delta q}{T}$ is true then it must also be the case that:

$$\frac{\Delta q_{\text{vap}}}{T_{\text{vap}}} \gg \frac{\Delta q_{\text{melt}}}{T_{\text{melt}}}$$

Water vaporization requires a lot of heat ($\Delta q_{\text{vap}} = +41.7 \text{ kJ/mol}$) at a moderately high temperature ($T_{\text{vap}} = 373 \text{ K}$). Melting ice occurs at a lower temperature ($T_{\text{melt}} = 273 \text{ K}$) but doesn't require nearly as much heat ($\Delta q_{\text{melt}} = +6.0 \text{ kJ/mol}$). Consequently:

$$\frac{\Delta q_{\text{vap}}}{T_{\text{vap}}} = 112 \text{ J/K} \gg 22 \text{ J/K} = \frac{\Delta q_{\text{melt}}}{T_{\text{melt}}}$$

Thus, Equation 4.1.1 for entropy makes sense.

As further proof, we contend that the entropy of vaporization: $\Delta_{\text{vap}} S = S_{\text{gas},m} - S_{\text{liq},m}$, ought to be nearly the same for most chemical substances. This is because gases have a very high entropy while liquids have significantly less. Furthermore, gases have very similar behavior as revealed by the near universality of the perfect gas law (meaning that $PV=nRT$ works regardless of the gas's chemical identity). As a result, the difference between the entropy of a gas and liquid ($\Delta_{\text{vap}} S$) should likewise be nearly universal. Shown in Figure 4.1 is the enthalpy of vaporization $\Delta_{\text{vap}} H_m$, which is the heat exchange (Δq_{vap}) necessary to boil a substance at constant pressure, versus the boiling (vaporization) temperature T_{vap} for ~100 chemicals. If our definition of the change of entropy is correct: $\Delta_{\text{vap}} S_m = \frac{\Delta_{\text{vap}} H_m}{T_{\text{vap}}}$, then we expect linear behavior between the heat and temperature via:

$$\Delta_{\text{vap}} H_m = \Delta_{\text{vap}} S_m \times T_{\text{vap}}$$

Clearly Figure 4.1 is a line with a slope of ~10.5 R, something that was noted back in 1884 by Frederick Trouton, an undergraduate student in Trinity College. Today we state that the entropy of vaporization of most chemicals is ~10.5 R, which is known as Trouton's Rule.

Next, we ascertain whether entropy is a state function, which as explained in sec. 2.2 means that the entropy content of a system is independent of how the system was prepared. As a result, if entropy is a state function, then a change of entropy is independent of how the change occurs (so called "path independence"). It would seem at first that this is unlikely, because heat itself is path dependent which is why the partial change in heat ∂q is an inexact differential as explained in sec. 2.4. It seems that $\frac{\partial q}{T}$ might likewise be inexact. Let's see if it is by applying Euler's test for exactness:

$\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$ Starting with:

$$\partial U = \partial q + \partial w$$

we will assume a reversible path is followed ($\partial w = -P\partial V$) because ∂U is exact and it is legit to use any path we want. We will also insert $C_V \partial T$ for ∂U . Some rearrangement yields:

$$\partial q = C_V \partial T + P \partial V$$

Dividing by T yields:

$$\frac{\partial q}{T} = \frac{C_V}{T} \partial T + \frac{P}{T} \partial V$$

When we juxtapose the above against the definition of a change of a function $\partial f = \left(\frac{\partial f}{\partial x} \right)_y \partial x + \left(\frac{\partial f}{\partial y} \right)_x \partial y$:

we see that $f = \frac{q}{T}$, $x = T$, $y = V$, $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$ and $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$.

When the Euler test for exactness: $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$ is applied to $\frac{\partial q}{T}$ using these definitions:

$$\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$$

The right-hand term can be evaluated as: $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$ since $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$, and using the perfect gas law we can show that: $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$ Pa/K².

The left-hand side: $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$ requires more examination. We are going to work this derivation in a slightly more complex fashion this time by ignoring the fact that $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$, and instead note that $\partial U = \partial q$ at constant volume because no work is done. Dividing by temperature means $\frac{\partial U}{T} = \frac{\partial q}{T}$, which makes the left side: $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$. Next we can switch the order of differentiation from $\frac{\partial}{\partial V} \frac{\partial}{\partial T}$ to $\frac{\partial}{\partial T} \frac{\partial}{\partial V}$ since U is exact:

$$\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$$

which is an application of the Euler Test. It turns out that $\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right) = 0 \text{ J/K}^2$ because at constant temperature $\partial U = 0 \text{ J}$ (and thus the numerator $\frac{\partial U}{T}$ is likewise 0 J/K). Consequently, we can rework the left-hand side of the Euler test as:

$$\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$$

Note that the units of J/K²/m³ are the same as (Pa/K²) from the right-hand side of the Euler test. Thus, $\frac{\partial q}{T}$ is exact because it passes the test, here:

$$\left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \right) = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \right)$$

Now that we are done making our eyes bleed due to the calculus, if it is acceptable that $\frac{\partial q}{T}$ is exact then we can accept that $\partial S = \frac{\partial q}{T}$ and $\partial q = T \partial S$. However, we had to use the reversible path when applying the Euler test to $\frac{\partial q}{T}$, and thus:

$$\partial S = \frac{\partial q_{\text{rev}}}{T} \quad (4.1.1)$$

This makes the change in entropy path independent, which must be the case if ∂S is exact.

The fact that $\partial q_{\text{rev}} = T \partial S$ reveals new thermodynamic relationships. For example, we can calculate the change ∂U for any reversible or irreversible process. However, as internal energy is a state function, changes in U can always be calculated using the reversible path even for irreversible transitions! Hence, $\partial U = \partial q_{\text{rev}} + \partial w_{\text{rev}}$, which means:

$$\partial U = T \partial S - P \partial V \quad (4.1.2)$$

Likewise:

$$\partial H = \partial U + \partial(PV) = T\partial S - P\partial V + P\partial V + V\partial P = T\partial S + V\partial P \quad (4.1.3)$$

which is the same as derived before (Equation ???) except here we incorporate Equation 4.1.2. This is also consistent with the fact that enthalpy is a state function, and as such ∂H can always be calculated using the reversible path. Equations 4.1.2 and 4.1.3 are very useful relationships that we will make much more use of in the future.

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