

# Introduction to Thermodynamics - What Happens when Salt meets Ice?

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## 1 Preface

In the following paper we will introduce various concepts from thermodynamics, and discuss the topic of why ice melts faster when in contact with salt. For first year students that have already completed their first year physics courses, this will be a very good preview of PHYS 203 or equivalent thermodynamics courses. For anyone that have taken a thermodynamics course, this paper can also be taken as a simple, but comprehensive review of the topic with a fun discussion on the side.

## 2 Preliminary Concepts

Before we why ice melts when in contact with salt. we will go through a few simple concepts which we will need to explain the phenomenon.

One of the core foundations of Thermodynamics lie in the concept of entropy. before getting into the specifics of a particle, we will look into the concept with an analogy. Imagine an arrangement of gambling chips of varying colours and values, including ones with "zero value". At any point in time the chips you have on hand will add up to a constant value, but it possible to swap chips for those of another colour granted the total value stays the same. A specific arrangement of colours is unique, and swapping one of the chips with one of another colour gives a different arrangement. To go further, imagine that not only do we just want to keep the total value constant, we also want to keep the total number of chips constant as well. There are only so many ways we can arrange the chips while fulfilling these condition. We can call this total number of arrangements  $\Omega$ .

We can change  $\Omega$  in two ways. One way to change  $\Omega$  is to add more chips, as the values associated with the new chip adds new arrangements. This case does not require a change in the total value. The second way is to increase the number of colours available, with the new colours creating new arrangements. Considering the existence of zero value chips, the initial  $\Omega$  should have arrangements using all chip values lower than our maximum. The only way to add new chip values then, is to increase the total value.

Going back to thermodynamics, the chips in the above example is attributed to particles, and the colours/values to the different energies the particles can have. And just as in the analogy, in a quantum setting, the different energies a particle can have is discrete. An arrangement as from before is called a micro-state of our system of particles.

The fundamental assumption of Thermodynamics is related to this, and states that every micro state has an equal probability of occurring.

If we were to bring two systems together, one with a number of micro states  $\Omega_A$  and another with a number of micro-states  $\Omega_B$ , the total number of micro-states with all the particles on the combined system is  $\Omega_A\Omega_B$ .

To get a value that we can associate with these two systems' number of micro-states that can be added linearly to get the associated value for the combined system, then, we will need to take the natural logarithm of the two  $\Omega$ 's. Further more, the logarithm will allow us to use sterling's formula, which allows us to get rid of the factorial from the  $\Omega$  calculations. Thus we define entropy as

$$S = k \log(\Omega) \quad (1)$$

where k is a constant of proportionality which converts the  $\log(\Omega)$  into appropriate units such as J/K or eV/K. For some unit systems, k is set to 1 then temperature and energy is then defined accordingly.

We can then consider the temperature of the system. We start by considering a small transfer of energy  $\delta E$  from  $E_B$  to  $E_A$  as the two systems of particles come into contact. Since the energy in each system changes, their respective entropy's also change. The change in  $\ln(\Omega_{AB})$ , written terms of  $E_A$  is then,

$$\Delta S_{AB} = \log(\Omega_A(E_A + \delta E)) + \log(\Omega_B(E_{tot} - (E_A + \delta E))) - \log(\Omega_A(E_A)) - \log(\Omega_B(E_{tot} - E_A))$$

where the first two logarithms give the entropy after the change in energy, and the second two for before the change (Without Boltzmann's constant k). If we plug the initial  $E_B$  in we have,

$$\begin{aligned} \Delta S_{AB} &= \log(\Omega_A(E_A + \delta E)) + \log(\Omega_B(E_B - \delta E)) - \log(\Omega_A(E_A)) - \log(\Omega_B(E_B)) \\ \Delta S_{AB} &= \log(\Omega_A(E_A + \delta E)) - \log(\Omega_A(E_A)) + \log(\Omega_B(E_B - \delta E)) - \log(\Omega_B(E_B)) \end{aligned}$$

In this situation, we can also have a  $dE_A = \delta E$  and  $dE_B = -\delta E$  from the direction of energy transfer, using this we can write,

$$dS_{AB} = \left( \frac{d \log(\Omega_A)}{dE_A} - \frac{d \log(\Omega_B)}{dE_B} \right) \times \delta E$$

and we notice, there is a point when 2 system in contact have the same change in entropy per change in energy,

$$\begin{aligned}\frac{dS_{AB}}{dE} &= \frac{d\log(\Omega_A)}{dE_A} - \frac{d\log(\Omega_B)}{dE_B} = 0 \\ \longrightarrow \frac{d\log(\Omega_A)}{dE_A} &= \frac{d\log(\Omega_B)}{dE_B}\end{aligned}$$

We call this critical point on the S vs E graph to be where the system is at thermodynamic equilibrium. Here we will introduce the concept of heat. In thermodynamics, heat is the quantity of energy transfer in or out of the system by means other than work or transfer of matter/particles. In the above example,  $dE$  is an example of this heat. Heat is denoted with  $Q$ , and a small increment with  $dQ$ . If we were to take the change in entropy for one system such that  $dQ = dE$ , we define temperature as

$$\frac{1}{T} = \frac{dS}{dQ} \quad (2)$$

This definition can be obtained by dimensional analysis.  $\frac{dS}{dQ}$  has units of  $\frac{1}{K}$  (or other temperature units that start from absolute zero in that sense), and it is clear where this result came from. This gives us an intuition of what temperature should be. Also directly from this, we can see that,

$$\frac{d\log(\Omega)}{dE} = \frac{1}{kT} = \beta \quad (3)$$

The above definition is where the Boltzmann's constant comes from, as it allows us to use the already existing measurement units of temperature and energy to quantify this relation.

The combined system will tend towards a distribution of energy such that  $\Omega_{AB}$  is maximized for the simple reason that since these distributions have higher  $\Omega_{AB}$ , they are more likely to occur. This tendency to reach a maximum supersedes the component system's entropy's. As long as  $\Omega_{AB}$  is maximized,  $\Omega_A$  and  $\Omega_B$  can and will change to accommodate. If in the process of this maximization the entropy of the universe increases, then the system will not spontaneously "reverse" back to its former state. On the other hand, if a universe maintains a constant entropy through the process, then it is reversible.

Going back to the thermodynamic equilibrium, the critical point we mentioned before would be a maximum and a stable equilibrium, as the overall system moves to reach a maximum  $S_{AB}$ . Furthermore at the point with,

$$\begin{aligned}\frac{d\log(\Omega_A)}{dE_A} - \frac{d\log(\Omega_B)}{dE_B} &= 0 \\ \longrightarrow \frac{1}{kT_A} - \frac{1}{kT_B} &= 0\end{aligned}$$

the temperatures of the 2 systems are equal. This meshes well with our intuition that two objects in contact will eventually reach the same temperature, just as with our two systems of particles.

Lastly, lets introduce a very useful relationship. Go back to entropy  $S = K \log(\Omega)$ . For a very small change in Energy  $dE$ , we have

$$\beta = \frac{d \log(\Omega)}{dE} \quad (4)$$

$$\frac{1}{T} dE = k d \log(\Omega) \quad (5)$$

$$\frac{dE}{T} = dS \quad (6)$$

here,  $dE$  is given by the heat  $Q$  and we have the very useful relationship:

$$dS = \frac{Q}{T} \quad (7)$$

when the process is reversible. As it is unnecessary for our present purposes, we will skip the calculations, but when a given process is irreversible then some energy will be wasted and

$$dS \geq \frac{Q}{T} \quad (8)$$

We will also introduce latent heat, which we will use briefly later. Latent heat is a experimentally determined value which measures the amount of heat required to undergo a phase transition per unit of mass,

$$L = \frac{Q}{m} \quad (9)$$

and for the latent heat for the ice to water transition is about 334J per gram of  $H_2O$ .

The reason we discuss latent heat is to discuss the Clausius-Clapeyron equation. But in order to introduce Clausius-Clapeyron equation, we also need to introduce the concept of Gibbs free energy, which is defined as,

$$G = U + PV - TS \quad (10)$$

where  $U$  is the internal energy of the system in question. It is the maximum amount a reversible that can be extracted from a thermodynamic system at constant pressure and temperature. So we have,

$$\Delta G = \Delta(U + PV - TS) \quad (11)$$

$$\Delta G = \Delta U + \Delta(PV) - \Delta(TS) \quad (12)$$

If pressure and temperature is held constant, as it normally would be in a phase transition, then we get

$$\Delta G = \Delta U + P\Delta V - T\Delta S \quad (13)$$

$$\delta G = \delta U + P\delta V - T\delta S \quad (14)$$

But if we hold V and S constant instead while P and T can vary, then

$$\delta G = \delta U + V\delta P - S\delta T \quad (15)$$

now we consider a P-T diagram, in which a phase diagram will be graphed.

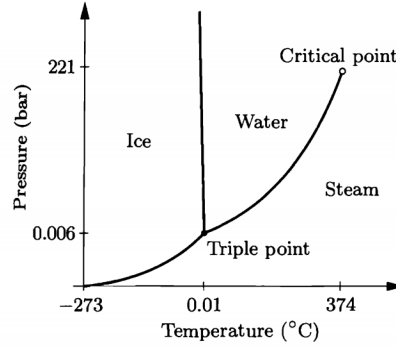


Figure 1: This is an example phase diagram. This phase diagram shows the phase transitions for water.

and consider approximating a small section of the line separating the two phases (e.g. solid and liquid) as a straight line. If we move along both sides of this small section,  $\delta P$  and  $\delta T$  are the same (since there is an identical displacement) and therefore  $\delta G$  is also the same on both sides. Then,

$$\delta G_s = \delta G_l \quad (16)$$

We know that P and T are varied, thus we use

$$\delta G = \delta U + V\delta P - S\delta T \quad (17)$$

While it was given before, we will state now that we state now that, with a constant number of particles, the change in internal energy can be given as,

$$dU = PdV - TdS \quad (18)$$

Since V and S are constant along the line,  $dU$  is also zero along the line. Then,

$$V_l \delta P_l - S_l \delta T_l = V_s \delta P_s - S_s \delta T_s \quad (19)$$

$$\longrightarrow \frac{\delta P}{\delta T} = \frac{S_l - S_s}{V_l - V_s} = \frac{\Delta S}{\Delta V} \quad (20)$$

which is the Clausius- Clapeyron equation.  $\Delta S$  and  $\Delta V$  is the change in entropy and volume when we "cross" the line, that is, when the system undergoes a phase transition. In the above equation, it is when it transitions from a solid to a liquid.

## 2.1 Relating Entropy to Quantum Mechanics

Our previous consideration of systems and their entropy's were made using two Einstein solids with  $N$  atomic bonds. The total energy of the solids is stored in those atomic bonds. These bonds can be thought of as slots for an indivisible or a discrete unit of energy aka quanta (out of the total energy).

Furthermore, this analogy can also be used in low-interaction fluids. Using the idea of potential in a space as an 'infinite square well', we can see that an ideal gas will also have possible energy states dependent on the volume of the space and the total energy distributed to the particle. An infinite square well is basically a particle inside a infinite potential barrier it cannot overcome, or in a more conventional setting, a particle in a rigid box where the box is a rigid body which will not deform. Then, in a one-dimensional infinite square well, we have

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (21)$$

And notice it complies with the idea of having specific quanta of energy. And when we have a low interacting fluid (i.e. an ideal gas) where the particles inside the fluid do not interact with each other, we can essentially view the particles as individual particles in a infinite square well which can receive different quanta of energy and be in different energy states. This is almost the same as an Einstein solids, except it may have a different energy spectrum and demonstrates that the same formulation of thermal physics can be applied to certain quantum-mechanical behaving system with minimal modifications. As for strongly interacting fluids, the system is much more complex and often cannot be easily understood using simple models, but often similar equations still applies, although not all of them will. This is why our previous explanation about entropy works without problem whichever matter phase our system may be.

## 3 Simple Explanation

Consider a system of an ice cube with some salt in contact. We denote the ice cube as  $H_2O_s$  and the salt as  $NaCl_s$ .

Initially some of the ice will melt into water ( $H_2O_l$ ) before we add the salt. At this point, the change in entropy from ice to water is:

$$\Delta S_{pure} = k \log(\Omega(H_2O_l)) - k \log(\Omega(H_2O_s)) \quad (22)$$

Once we add the salt, the salt dissolves into the water, while the ice has no interaction with the salt crystals. The addition of salt to the water causes the liquid portion of the system to experience a change in volume ( $\Delta V$ ) as we now have a salt and water mixture. The change in entropy from ice to water after mixing is then given by

$$\Delta S_{mixed} = k \log(\Omega(H_2O_l)) + k \log(\Omega(NaCl_{aq})) - k \log(\Omega(H_2O_s)) - k \log(\Omega(NaCl_s)) \quad (23)$$

Lets call this additional change in entropy due to the added salt,  $\Delta S_{mixed} - \Delta S_{pure}$ ,  $\delta S$  to distinguish from the  $\Delta S$  that happens when ice melt regardless if salt was added or not.

We start by considering the change in entropy ( $\Delta S$ ) contribution from the ice cube melting into water. A quick mental check reveals that  $\Delta S$  should be positive as water is more "chaotic" compared to ice, in which the molecules are held in place in a lattice.

Now we consider the calculation of the entropy more rigorously. We know that the latent heat of the ice to water transition,  $L = 334 J/g = \frac{Q}{m}$ , which implies  $Q$  is positive in this transition, and consider:

$$\Delta S \geq \frac{Q}{T} \quad (24)$$

thus when a certain amount of ice melts, it will result in

$$\Delta S \geq 0 \quad (25)$$

(this is without any salt added)

Now we consider an additional contribution cause by adding the salt. Which means we consider  $k \log(\Omega(NaCl_{aq})) - k \log(\Omega(NaCl_s))$ . We have  $\delta V(NaCl)$  which is  $V(NaCl_{aq}) - V(NaCl_s)$ . We can think of this change in volume as an increase of the number of available states for this system as there are much more spatial coordinates for the salt ions to occupy. We can also think of this using the 'particle in box' idea. As mentioned before, working with an 'infinite square well' we know that the energy states of such a system is as follows:

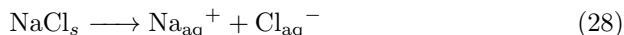
$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (26)$$

where  $L$  is the width of the well. This implies the energy state spacing is lower when the volume is increased, i.e. more available states for a fixed, and given energy. And for those of us who are less sophisticated, we can think of a gas

expanding in a empty box(i.e. vacuum). A gas expanding into a box will not spontaneous reverse the process and thus we can see the entropy must increase as volume increase.

$$\Omega(NaCl_{aq}) > \Omega(NaCl_s) \quad (27)$$

hence we know that the  $\Delta S$  contributed by the salt crystals turning into salt ions is positive. Furthermore, consider the dissociation equation:



We can see we have two types of distinguishable ions instead of one. We also have twice the numbers of particles after the crystals dissolve, which necessarily implies a positive contribution to the entropy.

Then  $\Delta S_{mixed} = \Delta S + \delta S$ , which means , adding salt increases the amount of  $\Delta S$  per amount of ice melting under constant temperature and pressure conditions. Which therefore drives the equilibrium towards favoring the liquid melting the ice. Following this logic, adding other kinds of solute substances should similarly increase the amount of  $\Delta S$  in the phase transition.

Another way to think about this is using the Clausius Clapeyron equation. The Clausius Clapeyron equation states that:

$$\frac{\partial P}{\partial T} = \frac{\Delta S}{\Delta V} \quad (29)$$

For a ice to water transition with salt know  $\Delta S$  increases, and  $\Delta V$  becomes less negative (since adding salt to increases the volume of water, which was lower than the volume of ice). We know that the slope of the ice/water phase transition is negative(water expands when freezing), thus the area of the liquid phase on the 3 phase diagram has expanded and freezing temperature lowered.

Further more, as ice have a very large latent heat, and so it will absorb heat from the surroundings during the above transition the surrounding temperature should lower as the ice melts.

## 4 Demo Analysis

The short attached video aims to demonstrate and expand on the concepts discussed in the previous sections. Note that the video is simply a demonstration not a rigorous experiment. The demonstration is mostly qualitative and shows a time lapse of three different systems melting.

In the demonstration, three systems were prepared; a system consisting with salt and ice, one with sugar and ice, and one with only ice. For the salt system and the sugar system, the additional substances were added as shown in



the video. It can be seen that the salt system reached a full liquid state in the shortest amount of time, which is 42 minutes and 53 seconds. The melting process for the sugar system took about 1 hour, 11 minutes, and 13 seconds to melt. The ice-only system took about 1 hour, 11 minutes, and 51 seconds to melt. Although the sugar system's melting time is very close to the ice-only system's melting time, the average temperature of the sugar and water solution throughout the process is lower than the average temperature of the water in the ice-only system; which implies that the sugar and water solution has a lower freezing point than water. Errors during the set-up stage could also have contributed to the similarity in melting time between the sugar system and the ice-only system. Since this is only a demonstration, these errors will not be discussed here. Notice that during the melting process for the salt system, the temperature dropped to as low as -2.1 degree Celsius in a relatively liquid dominated system whereas the other systems never reached temperatures that low. Overall, it can be seen that salt seems to make ice melt the fastest, followed by sugar. Qualitatively speaking, the solution from the salt system and the sugar system both have lower freezing points than pure water, and brine (salt-water solution) seem to have the lowest freezing point of the three.

Recall that when water comes in contact with salt, due to the increase in entropy of the liquid caused by the mixing will cause the liquid phase to be favoured and hence the phase equilibrium will shift to match. This change in equilibrium is why the freezing point shifts to a lower temperature, It is also important to briefly analyze the chemistry behind the cases with salt and with sugar. When either salt and sugar is added, the particles act as obstacles to the water particles when they would otherwise come together and form ice crystals. This obstacles slows the freezing of water, and also contributes to the shift in equilibrium.

Though the chemistry explanation only applies to specific combinations of substances, the physic-entropy explanation is generally true. As already explained in the explanation section, salt ( $\text{NaCl}$ ) splits into two ions when it mixes with the liquid water that is on the surface on the ice. Compared to sugar that doesn't split into ions, there are a larger number of particles per mole of salt added (and with the lower molar mass of salt, the same is true per mass) and this means each mole of salt added results in a larger change in entropy. Again, the reason for this is entropy and this might explain why salt has a larger effect than sugar.

In conclusion, it can be seen from the demonstration that when another substance comes into contact with ice (in this case salt or sugar), the ice melts faster due to the increase in entropy caused by the mixture at the molecular level. Because there is an entropy increase due to mixing, we can see from the Clausius Clapeyron equation that the freezing temperature of the resulting solution has to be lower than water. For the case of salt and sugar, it has also been observed to be so in the demonstration.