

The Boltzmann Factor

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Prerequisites

None.

Notes

None.

Document History

Date	Version	Comments
9th November 2017	1.0	Initial creation of the document.
17th January 2018	1.1	Adding the section on how the Boltzmann Factor changes with temperature.

1 The Boltzmann Factor

In statistical mechanics¹, the quantity

$$e^{-\frac{E}{kT}}$$

is known as the *Boltzmann Factor*. k is Boltzmann's constant, equal to roughly $1.38 \times 10^{-23} \text{ JK}^{-1}$, and T is the absolute temperature.

The kT in this expression actually represents the *average energy of particles in the system* we are looking at. Remember from Kinetic Theory that the average kinetic energy of particles in a gas came out to be $\frac{3}{2}kT$? Well, since there were a lot of simplifying assumptions in that theory, it may not be a surprise that this only gives us a *rough* idea of the average energy of particles in a gas. So let's forget about the number in front of the kT and think instead that roughly speaking, the average energy of particles in a system is kT .

So you could think about the Boltzmann Factor like this:

$$e^{-\frac{E}{E_{av}}}$$

where E_{av} is the average energy of the particles in the system.

Right. So now, let's explore a couple uses of the Boltzmann Factor.

2 The Probability of a Particle Having a High Energy

The first use is to determine the probability of a given particle in a system (which is at a temperature of T) having an energy greater than or equal to some cut-off energy, E_c . This turns out to be

$$p(E \geq E_c) = e^{-\frac{E_c}{kT}} \quad (1)$$

which is the Boltzmann Factor!

2.1 An Example

As an example, let's use a gas where $T = 290\text{K}$ (so that $kT = 4 \times 10^{-21} \text{ J}$), and see if we can work out the probability of a randomly chosen particle having energy greater than or equal to $kT = 8 \times 10^{-21} \text{ J}$ (that's *twice* the average energy). Well, that's easy: using (1),

$$\begin{aligned} p(E \geq 8 \times 10^{-21} \text{ J}) &= e^{-\frac{8 \times 10^{-21}}{4 \times 10^{-21}}} \\ &\approx 0.1353... \end{aligned}$$

That means that there would be roughly a 13.5% chance of finding that a randomly chosen particle had *twice* the average energy (*or more*) of all the particles.

Another way of saying this, of course, is that on average, around 13.5% of all particles have an energy that is at least twice the average.

2.2 Another Example

As another example, let's use the Boltzmann Factor, with average particle energy of E_{av} , and see if we can work out the probability of a randomly chosen particle having energy greater than or equal to $15E_{av}$. Well, using (1),

$$\begin{aligned} p(E \geq 15E_{av}) &= e^{-\frac{15E_{av}}{E_{av}}} \\ &= e^{-15} \\ &\approx 3.06 \times 10^{-7} \end{aligned}$$

¹Whatever *that* is!!

That means that there would be roughly a 0.00003% chance of finding that a randomly chosen particle had *fifteen* times the average energy (*or more*) of all the particles.

Another way of saying this, of course, is that on average, around 0.00003% of all particles have an energy that is at least fifteen times the average. Now that doesn't sound like a lot, does it? But if we applied this to one mole of a gas, which has 6.02×10^{23} particles in it, then that corresponds to 1.84×10^{17} particles!! That's a *huge* number of particles.

Why is this significant? Well, if you had a liquid, where the average energy of the particles is E_{av} , and let's say that the energy required for a particle to escape the liquid (by evaporation) was $15E_{av}$ (or more), then what this tells us is that an enormous number of particles in the liquid would have this energy of $15E_{av}$ (or more). So, as there are billions of collisions each second for a given particle(!), then evaporation would occur at a considerable rate. And since these high energy particles leave the liquid, the liquid will cool quite rapidly, as the escaping particles are taking their high energy with them, out of the liquid.

This might be quite surprising at first. You might think that if the energy required for a given process to occur was fifteen times the average energy of the particles in a system, then it could never happen. But the Boltzmann Factor tells us that the total energy of all the particles in a system is distributed in such a way that there are considerable numbers of particles with energies below the average, and considerable numbers of particles with energies *much* greater than the average, too.

3 Comparing the Numbers of Particles at Two Different Energies

It turns out that the number of particles having energy E in a system is given by

$$n(E) = Ae^{-\frac{E}{E_{av}}} \quad (2)$$

where $n(E)$ is the number of particles with energy E , and the average energy of all the particles is E_{av} . The coefficient A depends on things like the number of particles in the system, their masses, the average energy, and so on. But for the situations we are looking at, it will be a constant for a particular system.

Let's say we pick two different energies, E_1 and E_2 , and we are interested in comparing the numbers of particles at those energies. Well, we know that for energy E_1 ,

$$n(E_1) = Ae^{-\frac{E_1}{E_{av}}} \quad \text{or} \quad Ae^{-\frac{E_1}{kT}} \quad (3)$$

and for energy E_2 ,

$$n(E_2) = Ae^{-\frac{E_2}{E_{av}}} \quad (4)$$

Now if we divide (3) by (4) we will get

$$\frac{n(E_1)}{n(E_2)} = \frac{Ae^{-\frac{E_1}{E_{av}}}}{Ae^{-\frac{E_2}{E_{av}}}}$$

But the right hand side of this equation simplifies quite a bit:

$$\begin{aligned} \frac{n(E_1)}{n(E_2)} &= \frac{e^{-\frac{E_1}{E_{av}}}}{e^{-\frac{E_2}{E_{av}}}} \\ &= e^{-\frac{E_1}{E_{av}}} \times e^{\frac{E_2}{E_{av}}} \\ &= e^{-\frac{E_1 - E_2}{E_{av}}} \\ &= e^{-\frac{\Delta E}{E_{av}}} \end{aligned}$$

where ΔE is the *difference* between the energies.

3.1 An Example

As an example, let's take our gas, where the temperature of the gas is $T = 290\text{K}$, so that the average energy of the particles in the gas is $kT = 4 \times 10^{-21} \text{ J}$. If we were now interested in energies $E_1 = 1 \times 10^{-21}$, and $E_2 = 3 \times 10^{-21} \text{ J}$, then

$$\begin{aligned} \frac{n(E_1)}{n(E_2)} &= e^{-\frac{E_1-E_2}{E_{av}}} \\ \Rightarrow \frac{n(E = 1 \times 10^{-21})}{n(E = 3 \times 10^{-21})} &= e^{-\frac{1 \times 10^{-21} - 3 \times 10^{-21}}{4 \times 10^{-21}}} \\ &= e^{+\frac{2 \times 10^{-21}}{4 \times 10^{-21}}} \\ &\approx 1.65 \end{aligned}$$

And what this means is that there will be about 65% more particles with energy $1 \times 10^{-21} \text{ J}$ than there are with energy $E = 3 \times 10^{-21} \text{ J}$ in our gas.

So the Boltzmann Factor in the form

$$e^{-\frac{\Delta E}{E_{av}}} \quad \text{or} \quad e^{-\frac{\Delta E}{kT}}$$

gives you the ratio of the numbers of particles in energy states ΔE apart (the higher energy state having fewer particles, of course, because from Equation (2), the numbers of particles with energy E goes down as the energy E goes up).

4 How the Boltzmann Factor Varies with Temperature

Figure 1 below shows how the Boltzmann Factor, $e^{-\frac{E}{kT}}$, varies with temperature T , for three different values of E : $E_V = 5.5 \times 10^{-21} \text{ J}$, a typical Van der Waals bond energy, $E_H = 3.0 \times 10^{-20} \text{ J}$, a typical Hydrogen bond energy, and $E_C = 1.5 \times 10^{-19} \text{ J}$, a typical Covalent bond energy.

Note the logarithmic T -axis.

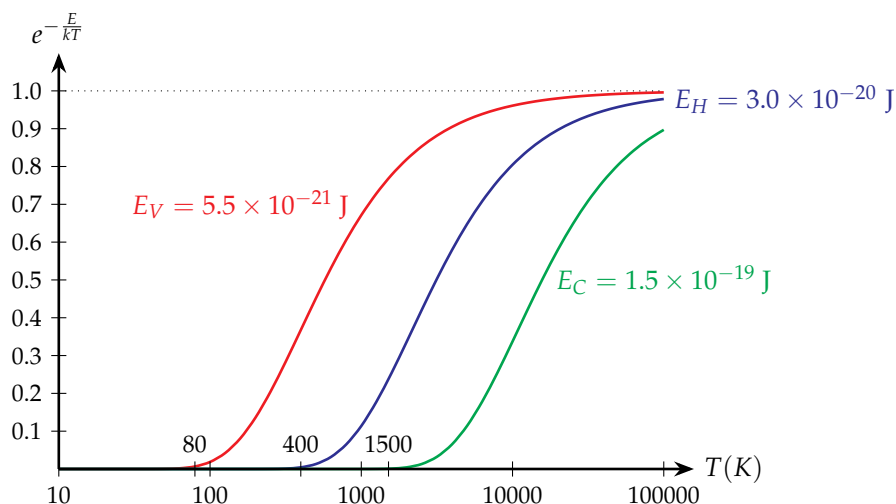


Figure 1: How the Boltzmann Factor Varies with Temperature

Things to notice:

- the three graphs all have the same form: for small T , the Boltzmann Factor is very small (effectively zero); as T increases there is a region where the Boltzmann Factor rises sharply; and for large T , the Boltzmann Factor approaches 1.0 asymptotically.
- the larger the value of E , the sharp rise in the Boltzmann Factor occurs in a higher range of temperatures.

How do we interpret these graphs?

4.1 Interpreting the Boltzmann Factor Graphs...

From what we found in Section 2, we can think of the y -axis of the graphs in Figure 1 as representing the probability of a particle in a system having the energy E or above.

And from Section 2.2 we know that as soon as the probability of particles having an energy greater than E rises above zero, processes that require this energy will start to occur. So, bearing that in mind...

4.1.1 ...for the Van der Waals Bond

So let's first consider the red line, representing the Boltzmann Factor at different temperatures for an energy that is typical of a Van der Waals bond.

At temperatures below around 80K, there will not be many particles in the system having an energy at or above the Van der Waals bond energy (as the Boltzmann Factor is effectively zero in this range). Consequently, for this temperature range, very few Van der Waals bonds will be broken due to the energies of the particles. Liquid Nitrogen (boiling point around 77K) would be an example of such a system: there are lots of Van der Waals bonds in liquid Nitrogen.

But as the temperature of the system rises, significantly more particles will have an energy greater than the Van der Waals bond energy. This means that more of the Van der Waals bonds will be broken. Well before 200K is reached, the probability of a particle having an energy greater than the Van der Waals bond energy is so high, *all* particles will have an energy sufficient to break a Van der Waals bond at some time or other. So no Van der Waals bonds will occur for very long at these temperatures.

This is why you don't find many Van der Waals bonds in a gas at room temperature and above.

4.1.2 ...for the Hydrogen Bond

The thinking here will be similar to that of the case of the Van der Waals bonds, except that the increasing probabilities of particles in the system having energies higher than the bond energy occurs at higher temperatures.

At temperatures below around 400K, there will not be many particles in the system having an energy at or above the Hydrogen bond energy. Consequently, for this temperature range, very few Hydrogen bonds will be broken due to the energies of the particles. Liquid water (boiling point around 373K) would be an example of such a system: there are lots of Hydrogen bonds in liquid water.

But as the temperature of the system rises, significantly more particles will have an energy greater than the Hydrogen bond energy, so more of the Hydrogen bonds will be broken. For rising temperatures, the probability of a particle having an energy greater than the Hydrogen bond energy is so high, *all* particles will have an energy sufficient to break a Hydrogen bond at some time or other. So no Hydrogen bonds will occur for very long at these temperatures.

This is why you don't find liquid water at temperatures exceeding around 400K.

4.1.3 ...for the Covalent Bond

The thinking here will be similar to that of the case of the Van der Waals and Hydrogen bonds, except that the increasing probabilities of particles in the system having energies higher than the bond energy occurs at higher temperatures.

At temperatures below around 1500K, there will not be many particles in the system having an energy at or above the Covalent bond energy. Consequently, for this temperature range, very few Covalent bonds will be broken due to the energies of the particles.

But as the temperature of the system rises, significantly more particles will have an energy greater than the Covalent bond energy, so more of the Covalent bonds will be broken. For rising temperatures, the probability of a particle having an energy greater than the Covalent bond energy is so high, *all* particles will have an energy sufficient to break a Covalent bond at some time or other. So no Covalent bonds will occur for very long at these temperatures.

Firing of ceramics is an example of this process: temperatures in excess of 1500K are required to drive out any water from and to melt the clay, which is held together by ionic and covalent bonds. As the clay cools and turns into a ceramic, different ionic and covalent bonds are created in the material, which turns out to have very different properties from the original wet clay.