

Lecture__09

October 10, 2022

1 The absolute scale of entropy?

The second law of thermodynamics introduced the concept of entropy, and that it either always stays constant or else increases for an isolated system. However, we don't know yet how to measure entropy, or what a typical value for it might be.

Consider again our definitions of heat capacities. We have that

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

and

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

From this, we have that

$$S = \int \frac{dQ}{T} = \int \frac{C_P}{T} dT$$

If we integrate this function, we end up with an undefined constant

$$S(T) = S(T_0) + \int_{T_0}^T \frac{C_P}{T} dT$$

In the test on Friday, we saw that measuring changes of S is possible, but figuring out an absolute measurement of entropy is not easy. This is what the third law of thermodynamics addresses.

2 The Third Law of Thermodynamics

There are two ways of arriving at a definition of the third law: statistically and experimentally. Let's start with the statistical definition.

2.1 Statistical

Consider a system which has distinct energy levels. If we enumerate over the energy levels without repetition, we have

$$E_1 < E_2 < E_3 < \dots < E_r < \dots$$

such that the degeneracy of level E_r is $G(E_r)$. The probability of the system being in a state with energy E_r is thus

$$P(E_r) = \frac{1}{Z} g(E_r) e^{-\beta E_r}$$

If the temperature of the system is low enough such that

$$E_2 - E_1 \gg k_B T$$

Then we'll have that

$$P(E_1) \approx 1, P(E_r) \approx 0$$

for all $r > 1$. Basically, we're saying that at low temperatures, we should only ever find the system to be in its ground state. The entropy of the system at these low temperatures must then satisfy

$$\lim_{T \rightarrow 0} S = k_B \ln g(E_1)$$

Although it has not been proven that $g(E_1) = 1$ for all systems (that is, the ground state for every system is non-degenerate), it holds for all cases that have been checked. This then means that

$$\lim_{T \rightarrow 0} S = 0$$

This leads quite nicely to Planck's statement of the third law, which is that

The entropy of all systems in internal equilibrium is the same as absolute 0, and may be taken to be zero

2.2 Classical

Let's consider the enthalpy and the Gibbs free energy again:

$$dH = TdS + VdP \tag{1}$$

$$dG = dH - TdS - SdT \tag{2}$$

If we perform a reaction in the lab (meaning it will be under constant temperature and pressure) we get the following information. First, change in enthalpy just becomes

$$\Delta H = \Delta Q$$

If $\Delta H < 0$, then heat is emitted from the system (exothermic reactions). If $\Delta H > 0$, then heat is absorbed into the system (endothermic reactions). For the Gibbs free energy, we found that under such conditions (constant T and P), $dG \leq 0$ - that is, the system will always try to minimise the Gibbs energy in order to reach equilibrium. As such, if for the reaction $\Delta G < 0$, it can occur spontaneously!

So, for such a reaction we have that

$$G = H - TS$$

This means that as the temperature approaches 0, the Gibbs Free energy and the enthalpy approach each other. This was experimentally proven by Walter Nernst, who then postulated that the entropy should go as $\Delta S \rightarrow 0$ as $T \rightarrow 0$. This led to the statement that

Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.

2.3 Consequences

2.3.1 Heat Capacity

So how does the 3rd Law affect all of the things we've talked about so far? First, let's consider heat capacity. Given that

$$C = T \left(\frac{\partial S}{\partial T} \right) = \left(\frac{\partial S}{\partial \ln T} \right) \rightarrow 0$$

as, when $T \rightarrow 0$, $\ln T \rightarrow \infty$ - so heat capacities go to 0 at 0 temperature!

2.3.2 Thermal Expansion

From Maxwell's equations, we have that

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

Since $S = S(T, P) \rightarrow 0$ as $T \rightarrow 0$ for all P, this implies that the left hand side of this equation also goes to 0. As such,

$$\lim_{T \rightarrow 0} \left(\frac{\partial V}{\partial T} \right)_P = 0$$

which also means that $\beta_P \rightarrow 0$. This means that thermal expansion stops.

With that, our discussion of the laws of classical thermodynamics comes to a close. Next, we're going to discuss statistical mechanics, and start looking at how we apply both classical and statistical thermodynamics to particular problems.

3 Equipartition of Energy

Before going further, we are going to discuss the equipartition theorem. To motivate our discussion, let's write down what the kinetic energy of a particle of mass m and moving a velocity v is

$$E_K = \frac{1}{2}mv^2.$$

Now, if we have a particle at the end of a spring, the potential energy of that particle when displaced by a distance x is

$$E_P = \frac{1}{2}kx^2$$

The total energy of a particle at the end of the spring is thus

$$E = E_K + E_P = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

As the particle oscillates back and forth, the energy within the system is constantly moving between kinetic energy and potential energy, while the total energy of the system remains constant. The interesting thing to note here is that both energy terms in this equation have a quadratic dependance on some variable (v^2 for kinetic, x^2 for potential).

Now let's imagine we have some system which is connected to a heat bath. The system is capable of extracting energy from the heat bath or transferring energy to it. What is the mean thermal

energy of the system? The thermal energy must be stored as either kinetic energy or potential energy - how exactly is it distributed?

So, let's assume we can write the energy down as some quadratic function - that is, we could write

$$E = \alpha x^2$$

where α is some constant and x is some variable. The probability that the system would have a particular energy αx^2 would then be

$$P(x) = \frac{e^{-\beta \alpha x^2}}{\int_{-\infty}^{+\infty} e^{-\beta \alpha x^2} dx}$$

where the bottom term is an integral rather than the normal summation we see in Z because we're going to assume here that x can have non-integer values. The mean energy of the system is then

$$\langle E \rangle = \int_{-\infty}^{+\infty} E P(x) dx \quad (3)$$

$$\langle E \rangle = \frac{\int_{-\infty}^{+\infty} \alpha x^2 e^{-\beta \alpha x^2} dx}{\int_{-\infty}^{+\infty} e^{-\beta \alpha x^2} dx} \quad (4)$$

$$\langle E \rangle = \frac{1}{2\beta} \quad (5)$$

$$\langle E \rangle = \frac{1}{2} k_B T \quad (6)$$

This is a pretty significant result, as even though we've assumed an arbitrary function for the energy, the mean energy that we get out just depends on temperature! It is possible (but non-trivial) to extend this result to allow for the energy to be made up of multiple quadratics, say

$$E = \sum_{i=1}^n \alpha_i x_i^2$$

then the result becomes

$$\langle E \rangle = \frac{n}{2} k_B T$$

This is a very, very useful theorem. Each quadratic term that contributes to the total energy is called a mode, or degree of freedom of the system. Thus, we get the theorem for the equipartition of energy:

If the energy in a classical system is the sum of n quadratic modes, and the system is in contact with a heat reservoir at temperature T , the mean energy of the system is given by $n k_B T / 2$

3.1 Applications

Translational motion in a monatomic gas:

$$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

Summation of 3 quadratic modes, meaning the mean energy of the system

$$\langle E \rangle = \frac{3}{2} k_B T$$

Rotational motion in a diatomic gas - that is, 2 particles bonded together that can then spin about 2 axes. This gives an additional 2 terms

$$\frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2}$$

This means the energy is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2}$$

and thus

$$\langle E \rangle = \frac{5}{2} k_B T$$

Vibrational energy in a diatomic gas - that is, imagine the 2 particles are bonded together with a spring. This adds gives another 2 terms:

$$\frac{1}{2}\mu(\mathbf{r}_1 - \mathbf{r}_2)^2 + \frac{1}{2}k(|\mathbf{r}_1 - \mathbf{r}_2| - l_0)^2$$

where k is an imagined spring constant, l_0 is the equilibrium molecular bond length, and μ is the reduced mass of the system. This means the total energy is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{1}{2}\mu(\mathbf{r}_1 - \mathbf{r}_2)^2 + \frac{1}{2}k(|\mathbf{r}_1 - \mathbf{r}_2| - l_0)^2$$

and thus

$$\langle E \rangle = \frac{7}{2} k_B T$$

Assumptions?