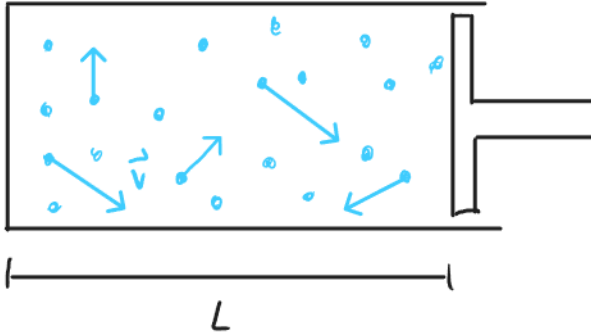


Physics 203 Notes

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Temperature is a measure of the tendency of an object to spontaneously give up energy to its surroundings.

Force of a monatomic ideal gas on a piston:



We assume all reflections off the walls are elastic and specular (specular implies that, $|v_x|, |v_y|, |v_z|$ are constant)

Before each collision with the piston, each particle will have velocity $\vec{v} = \langle v_x, v_y, v_z \rangle$ and after the collision, it will have a velocity of $\vec{v} = \langle -v_x, v_y, v_z \rangle$

So the change in velocity will be $\Delta \vec{v} = -2v_x \hat{i}$

The time period it takes for each particle to hit the piston and come back is given by

$$v_x = \frac{2L}{\Delta t} \Rightarrow \Delta t = \frac{2L}{v_x}$$

The force felt by each particle on the piston is given by

$$\vec{F} = \frac{d\vec{p}}{dt} = \frac{m\Delta \vec{v}}{\Delta t} = \frac{-2v_x \hat{i}}{\left(\frac{2L}{v_x}\right)} = -\frac{mv_x^2}{L} \hat{i}$$

This is just the force felt by 1 particle. If we want the force felt by all particles, we take the sum:

$$\vec{F} = \frac{m}{L} \sum^N v_x^2 \hat{i}$$

The formula for the expected value (average) of a population is given by

$$\langle x \rangle = \frac{1}{N} \sum^N x$$

We can apply this formula to our expression for force and rearrange

$$\frac{F}{N} = \frac{m}{L} \langle v_x^2 \rangle \Rightarrow F = \frac{Nm}{L} \langle v_x^2 \rangle$$

$$P = \frac{F}{A} = \frac{Nm}{AL} \langle v_x^2 \rangle = \frac{Nm}{V} \langle v_x^2 \rangle$$

We can assume that on average the particles are traveling with the same velocity in each direction

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

And so we can write the total velocity as

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle \Rightarrow \langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

$$P = \frac{Nm}{3V} \langle v^2 \rangle$$

$$PV = \frac{1}{3} Nm \langle v^2 \rangle$$

It was determined experimentally that $PV = Nk_B T$. These two results imply that

$$3k_B T = m \langle v^2 \rangle \Rightarrow \frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle = \langle K \rangle$$

So each quadratic degree of freedom (such as $\frac{1}{2}mv_y^2$) will have, on average $\frac{1}{2}k_B T$ of energy. So for an ideal gas that has f quadratic degrees of freedom, the average kinetic energy will be

$$\langle K \rangle = \frac{f}{2} k_B T$$

*For monatomic gasses, we will have $f = 3$ and for diatomic gasses $f = 5$.

State variables represent the state of a system, not how it got there. (i.e. they don't depend on the path).

Some state variables are T, P, V, U .

Any functions of only state variables are also state variables (e.g. $U + PV$)

For an *ideal gas* the internal energy of the gas will be the sum of the kinetic energy of each particle

$$U = \sum^N K$$

We derived earlier that

$$\sum^N K = \langle K \rangle N = \frac{f}{2} N k_B T$$

And so we get for an ideal gas the internal energy is

$$U = \frac{f}{2} N k_B T$$

In the case of an ideal gas, we were able to define U , however, in general U is often not well defined. This is because for non-ideal gasses the internal energy also consists of other energy such as chemical and nuclear energy.

The change in internal energy, ΔU , is often much better defined as is given by the general equation

$$\Delta U = Q + W$$

Q is energy added as heat, naturally flowing into the system due to a temperature difference.

W is work (energy) added to the system in some other form, even if it is directly converted to heat. (Microwaving something is an example of doing work on a system).

*Note the sign convention for W implies that positive work is energy that goes into the system from the surroundings.

Work done by a liquid/gas:

The definition of work is given by

$$W = \int \vec{F} \cdot d\vec{r}$$

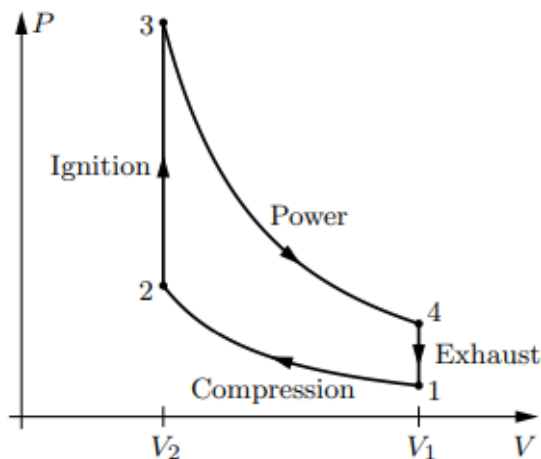
Using $P = \frac{F}{A}$, we can rearrange the equation to be in the form

$$W = - \int P(V) dV$$

*Note that the negative sign comes from our sign convention of work. Conceptually, if we want to have positive work added to the system we need to decrease the volume, meaning that dV would be a negative quantity, hence the sign flip in the equation.

The Otto cycle:

This is a common heat engine found in most automobiles.



1. Compression: An air-gas mixture is injected into the cylinder and is compressed adiabatically by a piston.

2. Ignition: A spark plug ignites the mixture, raising the temperature while the cylinder stays at a constant volume.
3. Power: The high pressure gas pushes the piston outward, expanding in volume and producing usable work.
4. Exhaust: The hot exhaust gasses are expelled and replaced by a new mixture of air and gas.

Note that because U is a state variable, it does not depend on paths so for a cyclic process such as the one described above, $\Delta U = 0$ for each cycle.

This implies that the net heat added to the system is equal to the net work done by the system.

$$Q_{\text{net}} = -W_{\text{net}}.$$

*For a heat engine we will have $Q_{\text{net}} > 0$ and $W_{\text{net}} < 0$ (it will be opposite for a refrigerator)

We can use this to calculate the efficiency of a heat engine as the net work out over the heat added to the system will give the efficiency

$$e = \frac{-W_{\text{net}}}{Q_h} = \frac{Q_h - |Q_c|}{Q_h} = 1 - \frac{|Q_c|}{Q_h}$$

Q_h and Q_c in this formula are the heat added and the heat expelled by the system respectively. ($Q_h > 0$ and $Q_c < 0$).

Microstate: the precise description of a state including specification of the value for each degree of freedom.

For example, if you flip three coins, the specific arrangement of those three coins (like HHT) will be a microstate.

Or for a single molecule of an ideal gas, a microstate will be the combination of values given by

$$\vec{r} = \langle r_x, r_y, r_z \rangle, \quad \vec{v} = \langle v_x, v_y, v_z \rangle$$

Macrostate: A set of states corresponding to some macroscopic characteristic, or set of characteristics.

For example, if we flip 3 coins, a macrostate would be the set of any microstates with 2 heads.

microstate	macrostate
HHH	3 heads
HHT	2 heads
HTH	2 heads
HTT	1 head
THH	2 heads
THT	1 head
TTH	1 head
TTT	0 heads

The multiplicity Ω of a macrostate is the number of microstates contained in that macrostate (the number of elements of the set if you will).

So for the above example we get $\Omega(3 \text{ heads}) = 1$ and $\Omega(2 \text{ heads}) = 3$

In general, the multiplicity of getting n heads from flipping N coins is

$$\Omega(n, N) = \frac{N!}{n!(N-n)!}$$

For very large systems, we are not always able to directly compute the factorials so we can make use of Stirling's approximation and simplify the result.

$$N! \approx \left(\frac{N}{e}\right)^N \sqrt{2\pi N}, \quad N \gg 1$$

For even larger N we can use a rougher approximation and omit the square root part:

$$N! \approx \left(\frac{N}{e}\right)^N$$

Another useful multiplicity to be able to calculate is that of an ideal gas with N atoms:

$$\Omega(N) = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (2mU)^{3N/2}$$

While multiplicities are particularly useful with respect to thermodynamics, it can make more sense at times to look at the probability of a macrostate.

The probability of a macrostate A can be represented as the multiplicity of event A divided by the total number of microstates. We can call this total number of microstates Ω_{total}

$$P(A) = \frac{\Omega(A)}{\Omega_{\text{total}}}$$

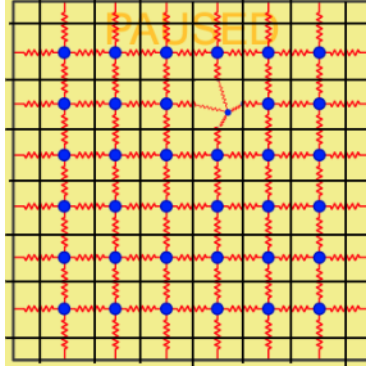
An important thing to note is the fundamental law of thermodynamics which states that all microstates are equally probable.

We can build toward connecting these ideas of multiplicity and thermodynamics by first introducing the concept of an Einstein solid. An Einstein solid is a theoretical idealization of a solid consisting of a collection of atoms that can oscillate in 3 directions (x,y,z) and don't interact with each other. Each oscillator will have a spacing of hf , where

$$f = 2\pi\sqrt{\frac{k_s}{m}}$$

and will have potential energy

$$U_s = \frac{1}{2}k_s x^2$$



We specify an Einstein solid by the number of oscillators, N , (the number of oscillators is 3 times the number of atoms) and the total quantized energy, q , that can be shared among these oscillators. For example, if we have an Einstein solid consisting of 6 oscillators (2 atoms) and 6 units of energy, we can share 1 unit in each oscillator, or 6 units in 1 oscillator and 0 in the others (this would be analogous to having one atom have a large amount of energy in the x direction and be stationary in the others).

The multiplicity of an Einstein solid is given by

$$\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!}$$

For an Einstein solid, N will be fixed and so the multiplicity will change depending on the amount of energy the solid has.

If we have two Einstein solids, A and B , that are coupled (think two objects in thermal contact) the system will have a total energy of $q_A + q_B$

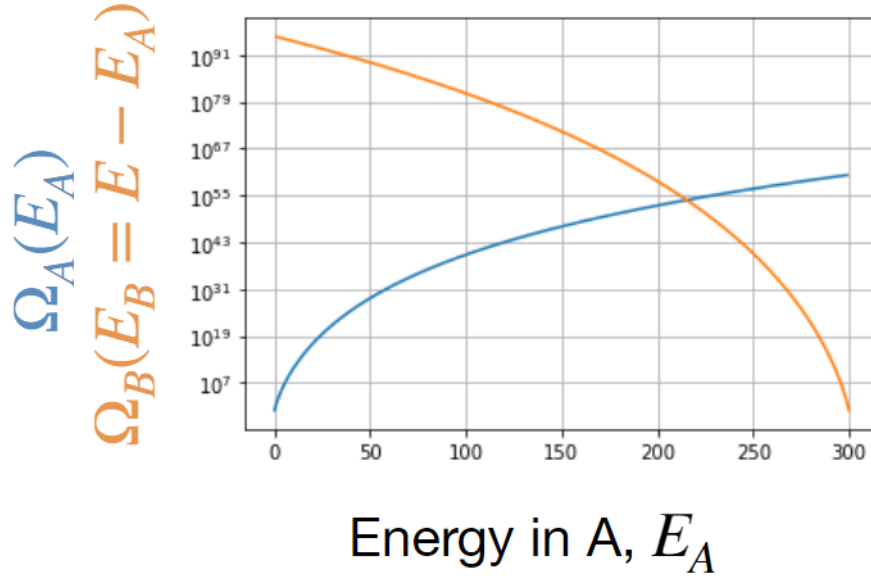
This will mean that the multiplicities of A and B will change depending on how we share the energy between the two solids.

The combined multiplicity of the system will be the product of the two individual multiplicities. So if we have N_A oscillators in A and N_B oscillators in B with E units of energy shared between the two of them then the combined multiplicity will be

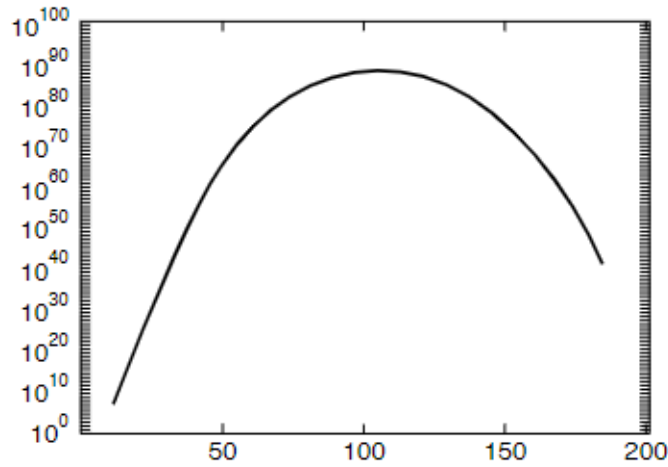
$$\Omega_{AB}(\epsilon_A) = \Omega_{\text{joint}}(\epsilon_A, E - \epsilon_A) = \Omega_A(N_A, \epsilon_A)\Omega_B(N_B, E - \epsilon_A)$$

For use of calculating probability, the total multiplicity will be given by

$$\Omega_{\text{total}} = \Omega(N_A + N_B, E)$$



When we multiply these two multiplicities, we get the joint multiplicity to look something like



Systems are most likely to be in macrostates with the highest Ω . If they start out in a macrostate with a lower Ω they will tend to evolve to the macrostate of highest Ω . (Think about how a system will try to establish thermal equilibrium).

This peak will occur where $\frac{d}{d\epsilon_A} \Omega_{\text{joint}}(\epsilon_A, \epsilon_B) = 0$

$$\frac{d}{d\epsilon_A} \Omega_j(\epsilon_A) = \frac{d}{d\epsilon_A} (\Omega_A(\epsilon_A) \Omega_B(\epsilon_B)) = 0$$

$$E = \epsilon_A + \epsilon_B \Rightarrow \epsilon_B = E - \epsilon_A$$

$$0 = \frac{d}{d\epsilon_A} (\Omega_A(\epsilon_A) \Omega_B(E - \epsilon_A))$$

$$0 = \frac{d\Omega_A(\epsilon_A)}{d\epsilon_A} \Omega_B(E - \epsilon_A) + \frac{d\Omega_B(E - \epsilon_A)}{d\epsilon_A} \Omega_A(\epsilon_A) = 0$$

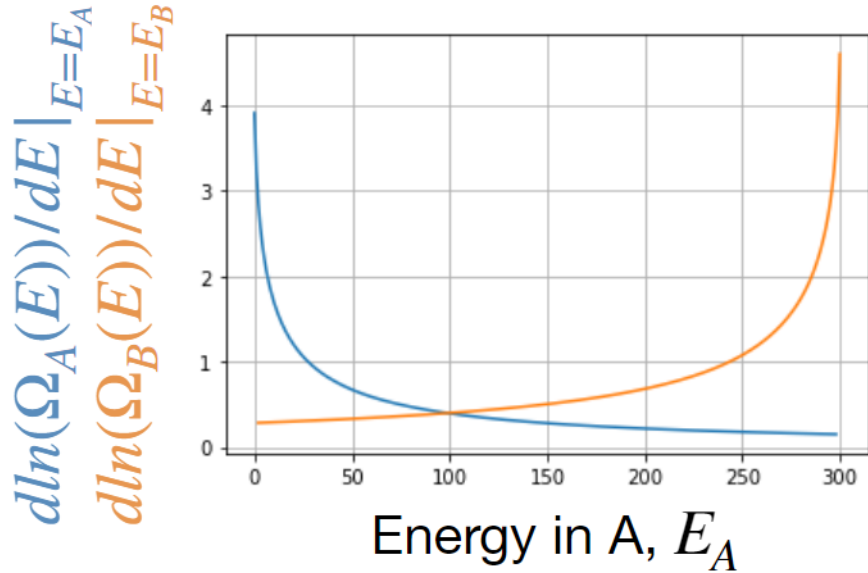
By chain rule we get that

$$\begin{aligned}\frac{d\Omega_B(E - \epsilon_A)}{d\epsilon_A} &= \frac{d\Omega_B(E - \epsilon_A)}{d(E - \epsilon_A)} \frac{d(E - \epsilon_A)}{d\epsilon_A} \\ \frac{d(E - \epsilon_A)}{d\epsilon_A} &= -1 \\ \Rightarrow \frac{d\Omega_B(E - \epsilon_A)}{d\epsilon_A} &= -\frac{d\Omega_B(E - \epsilon_A)}{d(E - \epsilon_A)} = -\frac{\Omega(\epsilon_B)}{d\epsilon_B}\end{aligned}$$

Going back to our original equation we get

$$\begin{aligned}\frac{d\Omega(\epsilon_A)}{d\epsilon_A} \Omega_B(\epsilon_B) - \frac{\Omega(\epsilon_B)}{d\epsilon_B} \Omega(\epsilon_A) &= 0 \\ \frac{d\Omega(\epsilon_A)}{d\epsilon_A} \Omega_B(\epsilon_B) &= \frac{\Omega(\epsilon_B)}{d\epsilon_B} \Omega(\epsilon_A) \\ \frac{1}{\Omega_A} \frac{d\Omega(\epsilon_A)}{d\epsilon_A} &= \frac{1}{\Omega_B} \frac{d\Omega_B(\epsilon_B)}{d\epsilon_B} \\ \frac{d \ln \Omega_A}{d\epsilon_A} &= \frac{d \ln \Omega_B}{d\epsilon_B}\end{aligned}$$

*This is also analogous to saying $T_A = T_B$.



We use this value of $\ln \Omega$ to define entropy:

$$S \equiv k_B \ln \Omega$$

This is known as the Boltzmann entropy. We can also define entropy in a slightly different way using Gibbs entropy which considers the probability of different macrostates.

$$S = -k_B \sum_i P_i \ln(P_i)$$

Boltzmann's definition of entropy is analogous to saying that the most probable macrostate of the system corresponds to the highest entropy of the system and so a system will always tend towards higher entropy based on probability. This leads to the 2nd law of thermodynamics:

Universal entropy will always tend to increase

Because of the 2nd law, we define processes to be either reversible or irreversible. Irreversible processes are those that create new entropy, and reversible ones are those that do not. In practice, no macroscopic process is perfectly reversible, although some processes come close enough.

Because we found that the derivative of entropy is related to temperature, we can now create a relationship between entropy and temperature:

$$\frac{1}{T} = \frac{dS}{dE}$$

Based on the result of the previous derivation, we can also define a new parameter, β , for ease of notation such that

$$\beta \equiv \frac{1}{k_B T} = \frac{d \ln \Omega}{d\epsilon}$$

Probabilities in a thermal reservoir:

Let's consider the situation where A is in thermal contact with a thermal reservoir, B , which is much larger than A . We are making the assumption that because B is so much larger than A , A is able to exchange energy with B without changing B 's temperature.

What is the probability of finding subsystem A having a certain macrostate, ψ that has energy ϵ_ψ . This corresponds to all the possible states that B can be in when A is in ψ . If the total energy of the joint system is E_j then the number of states B can be in is $\Omega_B(E_j - \epsilon_\psi)$. The probability is then

$$P_\psi = \frac{\Omega_B(E_j - \epsilon_\psi)}{\Omega_{\text{total}}}$$

$$\ln(P_\psi) = \ln(\Omega_B(E_j - \epsilon_\psi)) - \ln(\Omega_{\text{total}})$$

Using the fact that B is much larger than A , we can reasonably assume that $E_j \gg \epsilon_\psi$ and so we can make use of a Taylor expansion of the term $\ln(\Omega_B(E_j - \epsilon_\psi))$.

$$\ln(\Omega_B(E_j - \epsilon_\psi)) = \ln(\Omega_B(E_j)) - \epsilon_\psi \frac{d \ln(\Omega_B(E_j))}{d\epsilon} + \mathcal{O}(\epsilon_\psi^2)$$

$$\frac{d \ln(\Omega_B(E_j))}{d\epsilon} = \beta$$

$$\ln(\Omega_B(E_j - \epsilon_\psi)) = \ln(\Omega_B(E_j)) - \epsilon_\psi \beta$$

Going back to our original equation,

$$\ln(P_\psi) = \ln(\Omega_B(E_j)) - \epsilon_\psi \beta - \ln(\Omega_{\text{total}})$$

We can combine the terms $\ln(\Omega_B(E_j)) - \ln(\Omega_{\text{total}})$ to be some arbitrary constant, C .

$$\begin{aligned}\ln(P_\psi) &= C - \epsilon_\psi \beta \\ P_\psi &= e^C e^{-\epsilon_\psi \beta}\end{aligned}$$

We know that the probability of the sum of all states must be equal to 1

$$\begin{aligned}\sum_i P(\psi_i) &= 1 \Rightarrow \sum_i e^C e^{-\epsilon_{\psi_i} \beta} = 1 \\ e^C \sum_i e^{-\epsilon_{\psi_i} \beta} &= 1 \Rightarrow e^C = \frac{1}{\sum_i e^{-\epsilon_{\psi_i} \beta}}\end{aligned}$$

We can define this new sum in the e^C term to be the *partition function*, Z

$$Z \equiv \sum_i e^{-\epsilon_{\psi_i} \beta}$$

And so the probability is

$$P_\psi = \frac{e^{-\epsilon_\psi \beta}}{Z}$$

Now what if we wanted to calculate the average energy of this subsystem A . The definition of average is

$$\langle x \rangle = \sum_i x_i P(i)$$

With respect to energy, this would be

$$\langle \epsilon \rangle = \sum_j \epsilon_j P(j)$$

Plugging in the probability we calculated above we have

$$\begin{aligned}P(j) &= \frac{e^{-\epsilon_j \beta}}{\sum_i e^{-\epsilon_i \beta}} \\ \langle \epsilon \rangle &= \frac{\sum_j \epsilon_j e^{-\epsilon_j \beta}}{\sum_i e^{-\epsilon_i \beta}} \\ \text{note } \sum_j \epsilon_j e^{-\epsilon_j \beta} &= -\frac{d}{d\beta} \sum_j e^{-\epsilon_j \beta} = -\frac{dZ}{d\beta}\end{aligned}$$

$$\Rightarrow \langle \epsilon \rangle = -\frac{1}{Z} \frac{dZ}{d\beta} = -\frac{d \ln Z}{d\beta}$$

Average kinetic energy of a monatomic ideal gas:

We can start by writing out the energy of a single ideal gas atom:

$$\epsilon = \frac{1}{2} m |\vec{v}|^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

So an ideal gas will have a partition function of

$$\begin{aligned} Z &= \sum e^{-\frac{1}{2}(v_x^2 + v_y^2 + v_z^2)\beta} = \sum e^{-\frac{\beta m}{2} v_x^2} e^{-\frac{\beta m}{2} v_y^2} e^{-\frac{\beta m}{2} v_z^2} \\ Z &= \sum e^{-\frac{\beta m}{2} v_x^2} \sum e^{-\frac{\beta m}{2} v_y^2} \sum e^{-\frac{\beta m}{2} v_z^2} = \left(\sum e^{-\frac{\beta m}{2} v^2} \right)^3 \\ Z &= \left(\sum \frac{1}{\delta v} e^{-\frac{\beta m}{2} v^2} \delta v \right)^3 = \lim_{\delta v \rightarrow 0} \left(\frac{1}{\delta v} \sum e^{-\frac{\beta m}{2} v^2} \delta v \right)^3 = \lim_{\delta v \rightarrow 0} \left(\frac{1}{\delta v} \int_{-\infty}^{\infty} e^{-\frac{\beta m}{2} v^2} dv \right)^3 \\ Z &= \left(\lim_{\delta v \rightarrow 0} \frac{1}{\delta v} \sqrt{\frac{2}{m\beta}} \int_{-\infty}^{\infty} e^{-u^2} du \right)^3 = \left(\lim_{\delta v \rightarrow 0} \frac{1}{\delta v} \sqrt{\frac{2\pi}{m\beta}} \right)^3 \\ \ln Z &= 3 \ln \left(\lim_{\delta v \rightarrow 0} \frac{1}{\delta v} \sqrt{\frac{2\pi}{m}} \right) - \frac{3}{2} \ln \beta \\ \langle \epsilon \rangle &= -\frac{d \ln Z}{d\beta} = \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T \end{aligned}$$

For large systems we can write $\langle \epsilon \rangle = U$ and this fits with the equation for internal energy of an ideal gas we derived earlier.

Partition functions for composite functions:

For a system of two particles which do not interact and are distinguishable, we can identify that:

$$Z_{\text{total}} = Z_1 Z_2$$

However, if the particles are not distinguishable from each other, we can say that the total number of states is cut in half, so,

$$Z_{\text{total}} = \frac{1}{2} Z_1 Z_2 = \frac{1}{2} Z_1^2$$

We can expand this to a system of N particles as well.

For noninteracting, distinguishable systems

$$Z_{\text{total}} = Z_1 Z_2 Z_3 \cdots Z_N = \sum_{i=1}^N Z_i$$

For noninteracting, indistinguishable particles

$$Z_{\text{total}} = \frac{1}{N!} Z_1^N$$

Blackbody spectrum derivation:

We will start by calculating the number of modes of oscillation of electromagnetic radiation in a cavity of length L . In equilibrium, only standing waves are possible so we will have

$$\begin{aligned}\lambda_n &= \frac{2n}{L} \\ c &= \lambda f \\ f_n &= \frac{nc}{2L}\end{aligned}$$

If we use q to specify the number of photons in each mode then the energy for each mode will be given by

$$E_n = qhf_n = \frac{qhnc}{2L} = q\epsilon_n$$

The different microstates would be specified by the number of photons and so we can write the partition function as

$$Z_m = \sum_{q=0}^{\infty} e^{-\beta q\epsilon_m}$$

We can use the expression for a geometric sum to rewrite Z

$$\begin{aligned}\sum_{j=0}^{\infty} r^j &= \frac{1}{1-r} \\ Z_m &= \frac{1}{1 - e^{-\beta\epsilon_m}} \\ \text{recall } \langle E \rangle &= -\frac{d \ln Z}{d\beta} = -\frac{1}{Z} \frac{dZ}{d\beta} \\ \langle E_m \rangle &= \frac{\epsilon_m}{e^{\beta\epsilon_m} - 1}\end{aligned}$$

Expanding out we will have modes in 3 directions

$$\begin{aligned}\langle E_{n_x, n_y, n_z} \rangle &= \frac{hc|n|}{2L} \frac{1}{e^{\frac{hc|n|}{2L}} - 1} \\ E_{\text{total}} &= \sum_{n_x, n_y, n_z=1}^{\infty} \frac{hc|n|}{2L} \frac{1}{e^{\frac{hc|n|}{2L}} - 1} \\ |k| &= \frac{|n|}{2L} \\ E &= \sum_{k_x, k_y, k_z=\frac{1}{2L}}^{\infty} \frac{hc|k|}{e^{hc|k|} - 1} \\ E &= \frac{1}{dk_x dk_y dk_z} \sum_{k_x, k_y, k_z=\frac{1}{2L}}^{\infty} \frac{hc|k|}{e^{hc|k|} - 1} dk_x dk_y dk_z\end{aligned}$$

$$E = \frac{1}{dk_x dk_y dk_z} \int_0^\infty \int_0^\infty \int_0^\infty \frac{hc|k|}{e^{hc|k|} - 1} dk_x dk_y dk_z$$

Because the integrand only depends on $|k| = \sqrt{k_x^2 + k_y^2 + k_z^2}$, we can rewrite this nicely in spherical coordinates. When we convert to spherical, we'll have a conversion factor of $4\pi|k|^2$. Then we are integrating 1/8 of the sphere so we will also divide by 8

$$E = \frac{1}{dk_x dk_y dk_z} \frac{1}{8} \int_0^\infty \frac{hc|k|}{e^{hc|k|} - 1} 4\pi|k|^2 d|k| = \frac{1}{dk_x dk_y dk_z} \int_0^\infty \frac{\pi hc}{2} \frac{|k|^3}{e^{hc|k|} - 1} d|k|$$

If we change k back to n and ϵ we have

$$E = \frac{1}{dk_x dk_y dk_z} \int_0^\infty \frac{\pi}{2(hc)^3} \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon$$

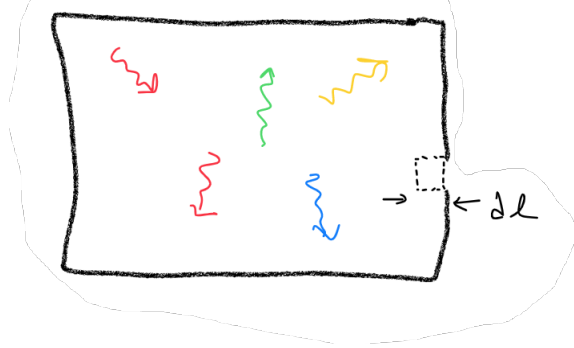
$$dk = \frac{1}{2L} \Rightarrow \frac{1}{dk_x dk_y dk_z} = 8L^3 = 8V$$

$$E = \int_0^\infty \frac{4\pi V}{(hc)^3} \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon$$

Note that because there are two possible polarizations of photons so the energy will be double this

$$E = \int_0^\infty \frac{8\pi V}{(hc)^3} \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon$$

We don't necessarily care about how much photon energy is in a box. We care more about how much leaves in the form of radiation.



The photons contained in the dashed box leave in time dt where $dl = cdt$ and $dV = Adl$

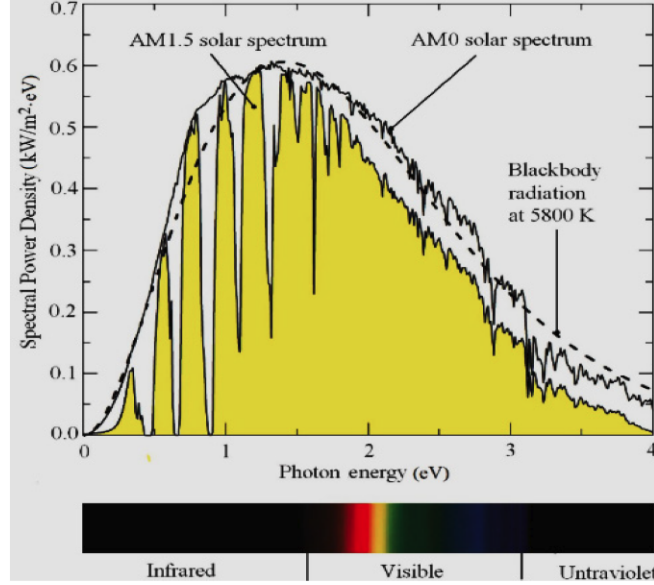
Note that only the photons moving to the right leave the box and the average x-velocity will be $\frac{c}{2}$ after averaging all angles.

$$dE = \frac{1}{4} E_{\text{total}} \frac{dV}{V} = \frac{E A c dt}{4V}$$

$$\frac{dE}{dt} = \frac{E A c}{4V} = \int_0^\infty \frac{2\pi A}{h^3 c^2} \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon$$

This rate of energy loss is known as *blackbody radiation* and will have units of Watts.

The integral from 0 to infinity gives the total power leaving. Often we are more interested in a particular range of wavelengths and would analyze a sliver of the spectrum shown below.



If we want to calculate the total power, we can do the following

$$P = \int_0^\infty \frac{2\pi}{h^3 c^2} \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon = \int_0^\infty \frac{2\pi}{h^3 c^2} \frac{1}{\beta^3} \frac{(\beta\epsilon)^3}{e^{\beta\epsilon} - 1} \frac{1}{\beta} d(\beta\epsilon)$$

$$P = \frac{2\pi}{h^3 c^2 \beta^4} \int_0^\infty \frac{u^3}{e^u - 1} du = \frac{2\pi}{h^3 c^2} (k_B T)^4 \frac{\pi^4}{15} = \sigma T^4$$

Heat capacities:

Earlier we derived that $\frac{1}{T} = \frac{dS}{dE}$. This was for two subsystems that could exchange energy but had no other affect on one another (they weren't changing volume or exchanging particles)

So to be more precise, we have the definition

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{N,V}$$

We can replace E with the internal energy as we are talking about the energy in the system. The subscript N, V means that we are holding the number of particles in the system and the volume of the system constant.

Heat capacity is how much heat must be put in to raise the temperature by a certain amount.

$$C = \frac{\delta Q}{dT}$$

In the case that we hold volume constant we will be dealing with constant volume heat capacity, C_V . We can start with $\Delta U = \delta Q + \delta W$. Because there is no change in volume, $\delta W = 0$. This means that $\Delta U = \delta Q$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

Relating this to entropy, we get

$$\begin{aligned}\frac{1}{T} &= \left(\frac{\partial S}{\partial U} \right)_{N,V} \Rightarrow \frac{\partial U_{N,V}}{T} = \partial S_{N,V} \\ \partial U_{N,V} &= \delta Q \\ C_V &= \frac{\delta Q}{\partial T_{N,V}} \Rightarrow \delta Q = C_V \partial T_{N,V} \\ \partial S_{N,V} &= \frac{\delta Q}{T} = \frac{C_V \partial T_{N,V}}{T}\end{aligned}$$

The 3rd law of thermodynamics states that when a system is in its lowest energy state, $\Omega = 1$, so $S = 0$.

However, there still exists residual entropy, where various crystalline structures may hold in place and take eons to rearrange to their zero state. This can also come from nuclear spins.

We can also know that $C_V \rightarrow 0$ as $T \rightarrow 0$.

We also have the following identity for pressure. I won't derive it here but one can check that it conceptually makes sense. If $\partial S/\partial V$ is large then the system wants to expand and will be scaled by a factor of T

$$P = T \left(\frac{\partial S}{\partial V} \right)_{U,N}$$

Using what we know, we can derive the thermodynamic identity

$$\begin{aligned}\Delta S &= (\Delta S)_1 + (\Delta S)_2 \\ \Delta S &= \left(\frac{\Delta S}{\Delta U} \right)_V \Delta U + \left(\frac{\Delta S}{\Delta V} \right)_U \Delta V \\ dS &= \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV \\ dS &= \frac{1}{T} dU + \frac{P}{T} dV \\ TdS &= dU + PdV\end{aligned}$$

$$dU = TdS - PdV$$

This statement is always true.

Relating this to $\Delta U = \delta Q + \delta W$, this statement is also always true due to conservation of energy. Comparing the two, one may notice that $W = -PdV$ and say that they are the same thing, however, this is not always true. $W = -PdV$ only holds for *quasi-static* processes.

Quasi-static means that the system has enough time to respond. An example of a non quasi-static process would be if you move a piston at the speed of sound. The atoms in the gas don't have time to get out of the way. Another example would be if a vacuum is suddenly introduced to the

system. In a non quasi-static system, δW is not well defined.

Relating this to adiabatic processes, an adiabatic process is defined to be where $\delta Q = 0$. A process that is both adiabatic and quasi-static is called *isentropic*.

We mentioned earlier that we can create new state variables as a combination of other state variables. We can do this to create new types of energy that relate to thermodynamic systems.

The first one we will start with is enthalpy, H .

Whereas U describes the energy needed to create a system out of nothing in empty space, H describes the energy needed to create a system in a finite-pressure atmosphere, pushing the surrounding environment out of the way.

$$H = U + PV$$

We can use this to define the heat capacity for a constant pressure process:

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

Throttling:

Throttling is a gas process with either rapid expansion or rapid compression of a gas. In such a case, there is either a “build up” or “void” of gas particles at the expansion/compression site, which causes the pressure to be not well defined at that point.

Because the process happens so fast, we say that $\delta Q = 0$, because there is not enough time for any heat transfer to take place. Therefore, we know that $\Delta U = \delta W$.

To obtain the work, we know that

$$\Delta U = U_f - U_i = P_f V_f - P_i V_i$$

Because the work required to push all of the gas on the high pressure side is $P_i V_i$ and the work required to “pull” all of the gas on the low pressure side is $P_f V_f$, in rearranging the equation, we get that,

$$U_f + P_f V_f = U_i + P_i V_i$$

$$H_f = H_i$$

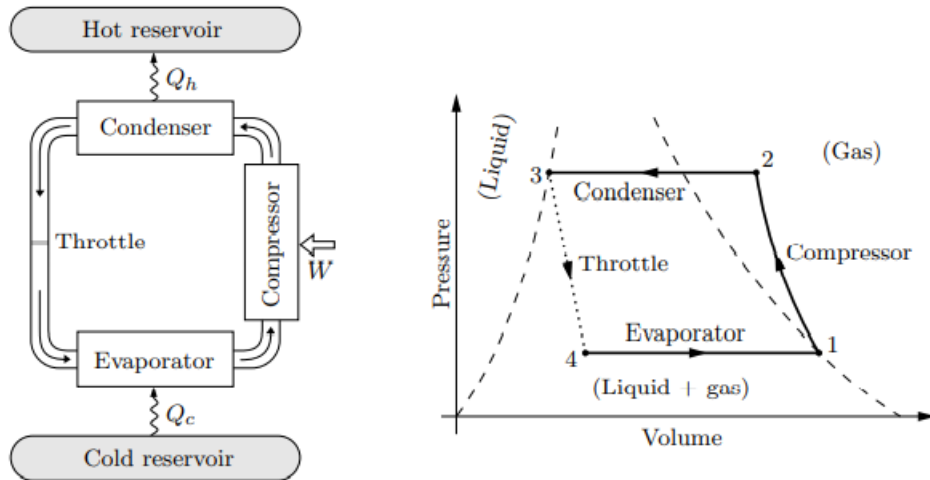
So we see that enthalpy is constant for a throttling process.

Because enthalpy for an ideal gas is characterized by

$$H = \frac{f+2}{2} N k_B T$$

We know that a constant enthalpy process is also constant pressure, which is why throttling doesn’t work well with ideal gases. The reason that non-ideal gases work better is because they have potential energy, ($H = U_{\text{potential}} + U_{\text{kinetic}} + PV$), which changes differently with temperature.

Refrigerator cycle:



1. Compressor: The gas is compressed adiabatically, raising its temperature and pressure. ($T \gg T_H$).
2. Condenser: The gas gives up heat and liquefies in the condenser. (The condenser is a network of pipes in contact with the hot reservoir).
3. Throttle: The liquid is then pushed through a throttling valve, lowering its temperature and pressure. ($T \ll T_C$).
4. Evaporator: The liquid absorbs heat from the cold reservoir and the process repeats

For a refrigerator we will have $W_{\text{net}} > 0$ and $Q_{\text{net}} < 0$. We will also have $Q_C > 0$ and $Q_H < 0$. The coefficient of performance of a refrigerator is the heat taken from the cold reservoir over the net work.

$$COP = \frac{Q_C}{W_{\text{net}}} = \frac{Q_C}{|Q_H| - Q_C}$$

We can also define another type of energy called *Helmholtz free energy*, F .

$$F = U - TS$$

If you're making the system from nothing in an external environment/reservoir at finite temperature, some of the energy required to make the system comes in as heat from the reservoir.

We can combine these ideas of H and F to define *Gibbs free energy*, G .

$$G = U + PV - TS$$

This is the energy required to create the system plus the work energy required to move the environment out of the way minus the heat energy that comes from the environment.

How systems evolve:

Let's look at the case in which a system can exchange heat energy with the environment but not work ($dV = 0$).

$$\begin{aligned}
dU_{\text{universe}} &= 0 = dU_{\text{system}} + dU_{\text{environment}} \\
dU_{\text{sys}} &= -dU_{\text{env}} \\
dS_{\text{uni}} &= dS_{\text{sys}} + dS_{\text{env}} \\
dU_{\text{env}} &= TdS_{\text{env}} - PdV_{\text{env}} \\
dV_{\text{env}} &= 0 \Rightarrow dU_{\text{env}} = TdS_{\text{env}} \Rightarrow dS_{\text{env}} = \frac{dU_{\text{env}}}{T} \\
dS_{\text{uni}} &= dS_{\text{sys}} + \frac{dU_{\text{env}}}{T} \\
\frac{dU_{\text{env}}}{T} &= -\frac{dU_{\text{sys}}}{T} \\
dS_{\text{uni}} &= dS_{\text{sys}} - \frac{dU_{\text{sys}}}{T} \\
dU_{\text{sys}} - TdS_{\text{sys}} &= -TdS_{\text{uni}} \\
F = U - TS &\Rightarrow dF = dU - TdS - SdT
\end{aligned}$$

If the system is at fixed temperature we'll have

$$\begin{aligned}
dT_{\text{sys}} &= 0 \\
dF_{\text{sys}} &= dU_{\text{sys}} - TdS_{\text{sys}} = -TdS_{\text{uni}}
\end{aligned}$$

The universe will evolve to maximum entropy. So for systems at fixed T and V , they will evolve to minimum F .

If we instead assume that $dV_{\text{env}} \neq 0$ but $P_{\text{sys}} = P_{\text{env}}$ and $dV_{\text{sys}} = -dV_{\text{env}}$

$$\begin{aligned}
dU_{\text{uni}} &= 0 = dU_{\text{sys}} + dU_{\text{env}} \Rightarrow dU_{\text{sys}} = -dU_{\text{env}} \\
dS_{\text{uni}} &= dS_{\text{sys}} + dS_{\text{env}} \\
dU_{\text{env}} &= TdS_{\text{env}} - PdV_{\text{env}} \\
dS_{\text{env}} &= \frac{dU_{\text{env}}}{T} + \frac{PdV_{\text{env}}}{T} \\
dS_{\text{uni}} &= dS_{\text{sys}} + \frac{dU_{\text{env}}}{T} + \frac{PdV_{\text{env}}}{T} \\
\frac{dU_{\text{env}}}{T} &= -\frac{dU_{\text{sys}}}{T} \\
\frac{PdV_{\text{env}}}{T} &= -\frac{PdV_{\text{sys}}}{T} \\
TdS_{\text{uni}} &= TdS_{\text{sys}} - dU_{\text{sys}} - PdV_{\text{sys}} \\
G = U - TS + PV &\Rightarrow dG = dU - TdS - SdT + PdV + VdP \\
dT &= dP = 0
\end{aligned}$$

$$dG_{sys} = dU_{sys} - TdS_{sys} + PdV_{sys}$$

$$dG_{sys} = -TdS_{uni}$$

So for systems with fixed temperature and pressure, the system will tend toward minimum G .

Chemical potential:

Let's take another look at the thermodynamic identity: $dU = TdS - PdV$. From this we can derive the following entropy drivers:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$$

This quantifies how much extra entropy a system gets by increasing the internal energy. (driver of energy exchange)

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}$$

quantifies how much extra entropy a system gets by increasing the volume. (driver of expansion)
Now suppose that particles can move into and out of a system. We will get

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

This quantifies how much extra entropy a system gains by adding extra particles. (driver of diffusion).

When $-\mu/T$ is large the system is very eager to pull in more particles to maximize its entropy.

Using this, we can now write the complete version of the thermodynamic identity as

$$dU = TdS - PdV + \mu dN$$

When $\mu_1 = \mu_2$, systems 1 and 2 are equally eager to attract more particles and so we say that the systems are in *diffusive equilibrium* (similar to how when $T_1 = T_2$ we have thermal equilibrium). This new term will come up when we are looking at the changes in different types of energy.

For example

$$dG = dU + VdP + PdV - TdS - SdT$$

$$dG = TdS - PdV + \mu dN + VdP + PdV - TdS - SdT$$

$$dG = \mu dN + VdP - SdT$$

From this we can derive the following differentials of G

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{N,T}, \quad S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}$$

Recall that for fixed T and P , G will tend to decrease. With fixed T and P we will have $dG = \mu dN$ and so particles will want to move to subsystems with lower μ .

For example, ice melts because $G_{\text{liquid}} < G_{\text{solid}}$ at $T < 0^\circ\text{C}$ so the molecules move from ice to water. We can now define a new type of energy called grand free energy, Ψ . With a reservoir that can supply both energy and particles Φ tends to decrease. Grand free energy is defined as

$$\Phi \equiv U - TS - \mu N$$

Expansion of gas:

The entropy of an ideal gas is given by the Sackur-Tetrode equation

$$S = Nk_B \left(\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right)$$

For fixed N and U , we can find the change in entropy

$$S = Nk_B \ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} Nk_B = Nk_B \ln \left(\frac{1}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{\frac{3}{2}} \right) + Nk_B \ln V + \frac{5}{2} Nk_B$$

$$\Delta S = Nk_B \ln V_2 - Nk_B \ln V_1 = Nk_B \ln \left(\frac{V_2}{V_1} \right)$$

Entropy of mixtures:

When a gas expands by a factor of X it will have an entropy of

$$S_f = S_i + Nk_B \ln X$$

So if a gas doubles in volume, the entropy will increase by $Nk_B \ln 2$

We can use this concept to help calculate the entropy of a gas mixture.

Say we have a gas comprised of two types of particles, A and B , that don't interact with one another.

Let's set x to be the percent of molecules of A in the mixture and let's also assume that all molecules take up the same amount of space.

$$x = \frac{N_A}{N_{\text{total}}} = \frac{V_A}{V_{\text{total}}}$$

$$1 - x = \frac{N_B}{N} = \frac{V_B}{V}$$

We can use the same calculations we used for expansion of a gas and use superposition of the two gasses to get

$$S_f = S_i + xNk_B \ln \left(\frac{1}{x} \right) + (1 - x)Nk_B \ln \left(\frac{1}{1 - x} \right)$$

$$S_f = S_i - Nk_B (x \ln x + (1 - x) \ln(1 - x))$$

We can also calculate the free energy of mixtures:

$$G_{\text{total}} = xG_A + (1 - x)G_B$$

Combining these results, and assuming constant T and P , we have

$$G_f = U_f + PV_f - TS_f$$

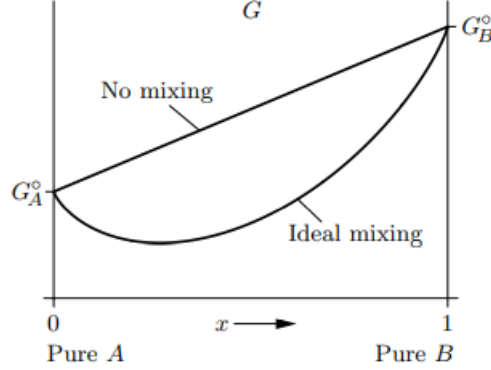
$$G_i = U_i + PV_i - TS_i$$

$$V_f \approx V_i, U_f \approx U_i$$

$$\Delta G = -T\Delta S$$

$$G_{\text{mixture}} = G_{\text{total}} + \Delta G$$

$$G = xG_A + (1-x)G_B + Nk_B T (x \ln x + (1-x) \ln(1-x))$$



In the above diagram, A has a lower Gibbs free energy than B, however, some mixture of A and B has the absolute lowest Gibbs free energy so the system will tend towards this mixture.

Dilute solutions:

For a system of all A, it will have Gibbs free energy $G_0 = N_A \mu_0$. (μ_0 is specifically for a system of all A). If we add a single particle of type B to the system, it will interact with the surrounding A particles, affecting dU and dV (does not depend on N_A). So we can write G of the system as

$$G = G_0 + dG = G_0 + dU + PdV - TdS$$

We will also have $dS = dS_1 + dS_2$ where dS_1 comes from the interaction between particle B and the surrounding A particles and dS_2 comes from the different locations that particle B can be found in. We will have

$$dS_2 = k_B \ln N_A$$

So if we write out the expression for dG again, we have

$$dG = dU + PdV - TdS = dU + PdV - TdS_1 - k_B T \ln N_A$$

We can see that the $dU + PdV - TdS_1$ term can be expressed as some function of T and P but not N_A and so we can write it as

$$dG = f(T, P) - k_B T \ln N_A$$

If we now introduce a 2nd B particle into the system, the expression will become

$$dG = 2f(T, P) - k_B T \ln N_A + k_B T \ln 2$$

The $k_B T \ln 2$ term comes from removing the incorrect extra multiplicity from swapping identical B particles.

Generalizing this to introducing N B particles, we get

$$dG = N_B f(T, P) - N_B k_B T \ln N_A + k_B T \ln(N_B!)$$

Using Stirling's approximation to get rid of the factorial and reintroducing the G_0 term, we get that

$$G = G_0 + dG = N_A\mu_0 + N_Bf(T, P) - N_Bk_BT \ln N_A + N_Bk_BT \ln N_B - N_Bk_BT$$

We can also get that

$$\begin{aligned}\mu_A &= \left(\frac{\partial G}{\partial N_A} \right)_{T, P, N_B} = \mu_0 - \frac{N_Bk_BT}{N_A} \\ \mu_B &= \left(\frac{\partial G}{\partial N_B} \right)_{T, P, N_A} = f(T, P) - k_BT \ln N_A + k_BT \ln N_B + k_B - k_B = f(T, P) + k_BT \ln \left(\frac{N_B}{N_A} \right)\end{aligned}$$

Looking at μ_B we can see that the system is *much* more eager to get additional B particles when there are almost none of them: $\frac{N_B}{N_A} \ll 1$ so $\ln \left(\frac{N_B}{N_A} \right) \ll 0$.

Putting it all together, we get that

$$\mu_A = \mu_0 - \frac{N_Bk_BT}{N_A}$$

This means that the system is mildly more eager to get additional A particles as a larger fraction of it becomes B particles.

It is easier to count mass (or moles) of solute (B particles) relative to mass (or moles) of solvent (A particles). This is called molality, m_B (or molarity). So rather than counting $N_A - N_B$ we have $m_B \propto \frac{N_B}{N_A}$. We can write $\frac{N_B}{N_A} = cm_B$ for some constant c .

$$\mu_B = f(T, P) + k_BT \ln c + k_BT \ln m_B$$

Osmotic Pressure:

Consider a system that is split in half by a membrane. On the left side there are some B particles diffused within a solution of A particles. On the right side, there are only A particles.

Initially, we will have

$$\begin{aligned}\mu_{L,A} &= \mu_0(T, P_L) - \frac{N_Bk_BT}{N_A} \\ \mu_{R,A} &= \mu_0(T, P_R)\end{aligned}$$

The red particles want to move to the left to decrease the G of the system. This means that the left pressure rises and the right pressure drops. This continues until $\mu_L = \mu_R$

$$\begin{aligned}\mu_0(T, P_L) - \frac{N_Bk_BT}{N_A} &= \mu_0(T, P_R) \\ \frac{N_Bk_BT}{N_A} &= \mu_0(T, P_L) - \mu_0(T, P_R) = (P_L - P_R) \frac{\partial \mu_0}{\partial P}\end{aligned}$$

We know $\mu_0 N_A = G_A$ so

$$\begin{aligned}\frac{\partial \mu_0}{\partial P} &= \frac{1}{N_A} \frac{\partial G_A}{\partial P} \\ G &= U + PV - TS \\ dG &= dU + PdV + VdP - TdS - SdT\end{aligned}$$

$$dU = TdS - PdV + \mu dN$$

$$dG = VdP - SdT + \mu dN$$

$$\frac{\partial G}{\partial P} = V$$

$$\frac{\partial \mu_0}{\partial P} = \frac{V}{N_A} = \frac{1}{n_A}$$

Where n_A is the numerical density of A.

And so we get

$$\frac{N_B k_B T}{N_A} = (P_L - P_R) \frac{1}{n_A}$$

$$P_L - P_R = n_A \frac{N_B}{N_A} k_B T = n_B k_B T = \frac{N_B}{V} k_B T$$

Chemical Reactions:

Consider a reaction, $A \rightleftharpoons B + C$. We will have $\Delta G(x) = -\mu_A(x) + \mu_B(x) + \mu_C(x)$ and the reaction will stop when $\Delta G = 0$.

$$\Rightarrow \mu_A(x) = \mu_B(x) + \mu_C(x)$$

We can use this to consider the dissociation of H_2O .



$$\mu_{\text{H}_2\text{O}}(x) \cong \mu_0^{\text{H}_2\text{O}}$$

$$\mu_{\text{OH}^-}(x) = k_B T \ln m_{\text{OH}^-} + \mu_0^{\text{OH}^-}$$

$$\mu_{\text{H}^+}(x) = k_B T \ln m_{\text{H}^+} + \mu_0^{\text{H}^+}$$

$$\mu_0^{\text{H}_2\text{O}} = \mu_0^{\text{OH}^-} + \mu_0^{\text{H}^+} + k_B T \ln m_{\text{OH}^-} + k_B T \ln m_{\text{H}^+}$$

$$\mu_0^{\text{H}_2\text{O}} - \left(\mu_0^{\text{OH}^-} + \mu_0^{\text{H}^+} \right) = k_B T \ln (m_{\text{OH}^-} m_{\text{H}^+})$$

Will give $-\Delta G$ for one complete reaction, to $m = 1$ products.

$$-\frac{\Delta G}{k_B T} = \ln (m_{\text{OH}^-} m_{\text{H}^+})$$

$$m_{\text{OH}^-} m_{\text{H}^+} = e^{-\frac{\Delta G}{k_B T}}$$

Using chemistry notation, we write it as

$$m_{\text{OH}^-} m_{\text{H}^+} = [\text{H}^+] [\text{OH}^-] = e^{-\frac{\Delta G}{k_B T}} \equiv K$$

We don't care about the concentration of H_2O because it is a pure liquid with no freedom in its concentration where as H^+ and OH^- are in solution. If we had a different reaction in which instead of H_2O we had $\text{A}_{(aq)} \rightleftharpoons \text{B}_{(aq)} + \text{C}_{(aq)}$ then we would've had $\mu_A(x) = k_B T \ln m_A + \mu_0^A$ which would give a solution of

$$\frac{[\text{B}] [\text{C}]}{[\text{A}]} = e^{-\frac{\Delta G}{k_B T}} = K$$

We can relate these ideas of entropy to information through information theory. The amount of information contained in some statement, Q , is the fraction of possibilities (before anything is known) that are eliminated, or the probability of the statement being correct with no information given.

We define the information contained in a statement s as

$$Q(s) \equiv -\log_2(P_s)$$

For states that are not all equally probable it resembles macrostates and entropy.

The Shannon entropy of a set of statements is

$$S_I = -\sum_s P_s \log_2 P_s$$

For uneven distributions, there is generally less information contained and there is room for information compression, while individual statements have uneven amounts of information, based on their probabilities.

Connecting this to entropy, we can say that the Boltzmann entropy, $S = k_B \ln \Omega$, is how much information is required to specify a certain microstate. The Gibbs entropy, $S = k_B \sum_i P_i \ln(P_i)$, is the amount of information it takes (on average) to specify a system under certain constraints (how much info does a system in a specific state contain).