

8 Enthalpy

Enthalpy is the total energy needed to create something. This is the energy of bringing together the constituent particles plus the energy needed to move the air out of the way to make room for the something.

$$H = U + PV$$

The enthalpy H is also the amount of energy that is liberated when the object is destroyed completely, for example in combustion. Enthalpy is defined and used widely because it is more experimentally accessible than is the internal energy U . Most experiments take place at constant pressure (one atmosphere). Therefore, the tables of measured enthalpy are typically taken to be constant pressure-enthalpies. Under this condition, we have

$$\Delta H = \Delta U + P\Delta V.$$

Recall the First Law: $\Delta U = Q + W$. The enthalpy is thus

$$\Delta H = Q + (-P\Delta V) + P\Delta V = Q$$

. The enthalpy of a process at constant pressure is simply the heat released in the process. So, we can easily measure enthalpies in calorimetry experiments.

Example: compare the cost per kcal of gasoline to that of corn flakes. The enthalpy of combustion of one gallon of gasoline is 31×10^4 kcal. The enthalpy of combustion of 28 grams of cornflakes is 100 kcal.

gasoline: One gallon of gasoline weighs about 6 lb, so has a mass of about $m = 2.7$ kg. So the heat of combustion for gasoline is 31×10^4 kcal/2.72 kg = 1.14×10^5 kcal/kg. Assuming gas runs about \$3/gallons, we find a cost of about \$1.10/kg. Each kg represents 1.14×10^5 kcal of available energy. Therefore, the price per kcal is 9.65×10^{-4} cents/kcal.

cornflakes: A 17 oz. box of cereal has a mass of around 482 g. At \$3/box, the price of cornflakes is around \$6.22/kg. Since each kg of cereal has 3571 kcal of available energy, we find a price per kcal of $(\$6.22/\text{kg})/(3571 \text{ kcal/kg}) = 0.17$ cents/kcal.

Cornflakes are about 180 times more expensive per kcal than is gasoline.

9 Chapter 2 Notes: The Second Law

Chapter 2 introduces *statistical mechanics*. Specifically, we will begin to understand the statistical foundation of entropy. You may find yourself agreeing with the Einstein quote on the syllabus regarding the second law of thermodynamics as the only physical law that will undoubtedly stand the test of time. To begin, let's define some related concepts:

- **Macrostate:** A macrostate describes an overall state of the system at hand in terms of macroscopic variables. Examples: The total energy in the room right now represents a particular macrostate. In a flip of 10 coins, the configurations that all yield four heads and six tails would belong to the "4-H" macrostate.
- **Microstate:** A microstate describes a specific configuration of microscopic variables. Examples: The room may be characterized by a particular energy (macrostate), but there are many (understatement) ways to arrange the energies of the individual molecules in the room to achieve the overall macrostate (total energy). Each of these arrangements represents a distinct microstate belonging to the same macrostate. With respect to the coin flip above, there are 210 ways to end up with 4 heads in a flip of 10 coins. Each of the 210 possible tosses is a separate microstate belonging to the 4H macrostate.
- **Multiplicity:** The Multiplicity function $\Omega(n)$ is a function of the macrostate n that returns (is equal to) the number of microstates in the given macrostate n . Example: $\Omega(4) = 210$ for the 10 coin flip above.

9.1 More with Coins

In a flip of three fair coins, the table below list all the macrostates, microstates, and associated multiplicities.

The total number of microstates available to the two-state system (HT) is the sum of all the $\Omega(n)$. Note that this is just 2^N where N is the number of coins. In the case of the table for the 3 coin flip, there are $2^3 = 8$ microstates.

In general, $\Omega(n)$ is the number of ways of choosing n heads in a given coin toss of N coins. We'll now find a useful formula for computing $\Omega(n)$. Hint: The formula we get is important!

- In a flip of 10 coins, how many ways are there of choosing the 1H state? $\Omega(1) = 10$.

Flip of Three Coins:

Macrostate	Microstate	Ω
0 H	TTT	1
1 H	TTH	3
1 H	THT	
1 H	HTT	
2 H	THH	3
2 H	HTH	
2 H	HHT	
3 H	HHH	1

Table 3: Ω counts the number of microstates belonging to a given macrostate

- How many ways are there of choosing the 2H state? 10 for the first coin, and then 9 for the second coin (because one of the ten is already flipped). So, $\Omega(2) = 10 \times 9$? Not quite - the coins could be chosen in any order, so we've actually over counted by a factor of 2. So, actually, $\Omega(2) = (10 \times 9)/2$.

- Similarly, there are

$$\Omega(3) = \frac{10 \times 9 \times 8}{3 \times 2}$$

ways of choosing the 3H state, and

- the 4H state can be chosen in

$$\Omega(4) = \frac{10 \times 9 \times 8 \times 7}{4 \times 3 \times 2}$$

ways.

The pattern that emerges defines the *choose* function:

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

9.2 Probability and Multiplicity

What is the probability of obtaining exactly 3 heads in a toss of 10 coins? The multiplicity $\Omega(3)$ tells us how many ways there are of getting 3 heads. So the probability is just

$$P(3H) = \frac{\Omega(3)}{\Omega(0) + \Omega(1) + \Omega(2) + \cdots + \Omega(10)} = \frac{\binom{10}{3}}{2^{10}} = \frac{120}{1024} = 0.1172$$

9.3 Some Practice Problems

Test your understanding of the material so far:

- Find the probability of getting 2 heads in a fair toss of 3 coins.

$$P(2, 3) = \frac{\Omega(2)}{2^3} = \frac{3}{8}$$

- Find the probability of getting 5 heads in a fair toss of 10 coins (first guess, then check your guess).

$$P(5, 10) = \frac{\Omega(5)}{2^{10}} = \frac{252}{1024} = 0.246$$

- Find the probability of getting 2 heads *twice* (2 flips of 2 coins)

$$[P(2, 3)]^2 = \left(\frac{3}{8}\right)^2 = \frac{9}{64}$$

- What is the probability of getting exactly one 6 in a roll of two dice? This is the *conditional* probability of one dice returning a 6 AND the other not returning 6:

$$P(6|\text{not } 6) = \frac{1}{6} \times \left(1 - \frac{1}{6}\right) = \frac{5}{36}$$

- Russian Roulette: What's the probability of being alive after 1 spin? 2 spins? 3? 4? 5?

– one spin:

$$P(\text{life}) = 1 - \frac{1}{6} = \frac{5}{6} = 83\%$$

– two spins:

$$P(\text{life}) = \left(\frac{5}{6}\right)^2 = 69\%$$

– three spins:

$$P(\text{life}) = \left(\frac{5}{6}\right)^3 = 58\%$$

– four spins:

$$P(\text{life}) = \left(\frac{5}{6}\right)^4 = 48\%$$

9.4 Poisson Distribution (not in text)

Recall the example of estimating the probability that all of the air in the room is found to be in a small volume in the corner. Before we worry too much about this possible but improbable scenario, let's calculate the probability of this occurring.

Problem Statement: We have N weakly interacting particles moving in a volume V . What is the probability of finding exactly n particles within some particular subvolume v of V ?

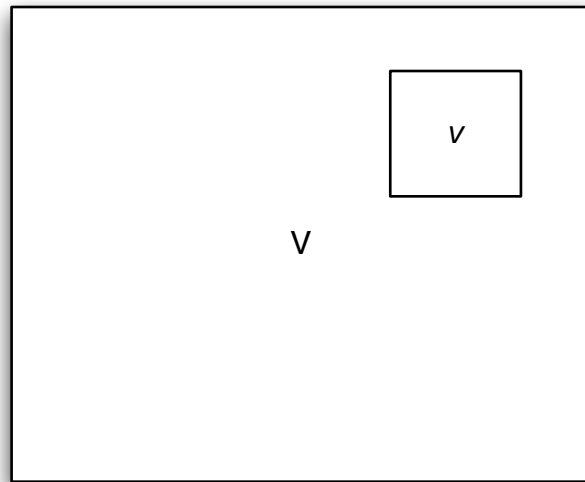


Figure 3: A volume V with a smaller subvolume v

- The probability of finding *one* particle in v is $p = v/V$.
- The probability of finding that one particle outside of v is then $(1 - p)$.
- The probability of finding a particular set of n particles in v is

$$P_v(n) = (\text{probability of finding one particle in } v)^n \times (\text{probability that the rest of the particles are found outside } v)$$

This is called *conditional probability* - the probability of an event is conditionally dependent on other events. We can then write:

$$P_v(n) = p^n (1-p)^{N-n}$$

Now there are $\binom{N}{n}$ ways to arrange the particles to have a set of n inside v and a set of $N-n$ outside v . Therefore,

$$P_v(n) = \binom{N}{n} p^n (1-p)^{N-n}$$

When $v \ll V$, we can simplify:

$$\binom{N}{n} = \frac{N!}{n!(N-n)!} \approx \frac{1}{n!} N^n \text{ Show this yourself}$$

Likewise, we can approximate $(1-p)^{N-n} \approx (1-p)^N$. Now $p \ll 1$, so we can expand $(1-p)^N$ according to $(1-x)^N \approx e^{-Nx}$. Therefore, we have the result

$$P_v(n) = \frac{(pN)^n}{n!} e^{-pN} \quad (61)$$

This is the famous *Poisson Distribution*.

Example: A glass of air holds $N = 3 \times 10^{25}$ molecules. What is the probability that 50% of them will be found in a subvolume v that is 1% of the original volume V ?

$$p = \frac{v}{V} = 10^{-2} \text{ and } n = 1.5 \times 10^{25}$$

$$\Rightarrow P_v(n) = \frac{(3 \times 10^{23})^{1.5 \times 10^{25}}}{(1.5 \times 10^{25})!} e^{-3 \times 10^{23}}$$

This is zero in any approximation scheme!

9.5 The Einstein Solid

The Einstein Solid is a purely notional model of a solid. It encompasses only the most essential features of the statistical-thermodynamics of a generic solid. Unlike most systems, the Einstein Solid permits a straightforward calculation of the multiplicity function Ω . It is a good pedagogical model, but should not be taken too seriously as a model of solids.

Recall that the basic picture of a solid material is of a lattice of quantum harmonic oscillators (QHO). Such oscillators have discrete and equally spaced energy levels. Since there are 3 unique vibrational modes for each lattice site, a model consisting of N QHO's might represent a solid with $N/3$ atoms. The relevant macrostate parameter is the total energy E of the solid. Consider a solid consisting of 3 atoms. The table of microstates up to energy $E = 3$ is given below. The text makes a heuristic attempt at deriving the multiplicity function for an Einstein solid with N oscillators and q units of energy:

$$\Omega(N, q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \quad (62)$$

Think about this formula. Does it make sense in terms of the example of a solid with three oscillators?

9.6 Interacting Systems

In this section of the text, we really get to the key idea of statistical mechanics. When two Einstein solids are brought into contact, what happens? Imagine that one solid (A) with $N_A = 3$ QHO's has $q_A = 4$ units of energy, while the other with $N_B = 3$ has $q_B = 2$ units of energy. Also, allow the two solids in contact to exchange energy with each other subject to the "energy conservation" constraint that the total energy of the two solids cannot exceed $q_A + q_B = 6$. What are the possible microstates of the composite solid? There are 462 possible states that the composite system might be found in. Is it possible that solid B (initially the cooler one) gives up all its energy to solid A (initially the hotter one) so that B cools further and A heats up? Yes - this scenario corresponds to the last set of multiplicities in the table ($q_A = 6$ and $q_B = 0$). There are 28 total microstates that each allow for B to give up all of its heat to A. The **Fundamental Assumption of Statistical Mechanics** is that all 462 microstates are equally probable.

In an isolated system in thermal equilibrium, all accessible microstates are equally probable

An Einstein Solid with $N = 3$ atoms:

Energy	QHO1	QHO2	QHO3	Ω
0	0	0	0	1
1	0	0	1	3
1	0	1	0	
1	1	0	0	
2	0	0	2	6
2	0	2	0	
2	2	0	0	
2	0	1	1	
2	1	0	1	
2	1	1	0	
3	0	0	3	10
3	0	3	0	
3	3	0	0	
3	2	1	0	
3	1	2	0	
3	0	2	1	
3	0	1	2	
3	1	0	2	
3	2	0	1	
3	1	1	1	

Table 4: Ω counts the number of microstates belonging to a given macrostate

Two Einstein Solid with $N = 3$ oscillators each and $q_A + q_B = 6$

q_A	Ω_A	q_B	Ω_B	$\Omega_{\text{Total}} = \Omega_A \Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28
total = 462				

Table 5: macrostates and multiplicities of a two-Einstein solid composite

So, yes it is possible that B gives up all its heat to A. But is it probable? *No*: Only 28 of the total 462 ($P = 28/462 = 0.06$) microstates correspond to this situation. So, it is not very likely. In the more realistic situation of a solid with 10^{25} oscillators sharing many more energy units, the probability of one of the solids giving up all its heat to the other is vanishingly small. So, thermal equilibrium, the flow of heat from a hotter to object to a cooler object, is a matter of probability, not certainty. But, the probability is more certain than any of the certainties we typically deal with!

9.7 Paramagnetic Solids

A paramagnetic material is one in which a magnetic dipole moment is induced only in the presence of an external magnetic field. A paramagnet loses its magnetic properties in the absence of the external field. Most materials are paramagnetic to some degree. We can model paramagnetic materials as a line of coins that can each be in one of two states - heads up or heads down. This two-state system is a good analogy because the electrons in a paramagnetic material can be either aligned with the external field or anti-aligned (spin-up or spin-down). If the paramagnet consists of N dipoles, then

$$N = N_{\uparrow} + N_{\downarrow}$$

We can translate our work with coins directly to the paramagnet with the equivalencies:

$$n \Rightarrow N_{\uparrow} \text{ and } N - n = N_{\downarrow}$$

With these substitutions, the multiplicity function for a paramagnet becomes:

$$\Omega(N, n) = \frac{N!}{N_{\uparrow}! N_{\downarrow}!}$$

We'll use this later when we look at the entropy of a paramagnetic material.

9.8 Stirling Approximation

Often (almost always in statistical mechanics), we are interested in systems for which $N > 10^{23}$. In this case, the multiplicity function can be simplified according to the Stirling Approximation. The derivation is in appendix B of the text, so I'm not going to duplicate it here. The result is

$$N! \approx (2\pi N)^{1/2} N^N e^{-N} \quad (63)$$

A more useful form of the Stirling formula is obtained by taking the logarithm of both sides of $N!$.

$$\log(N!) \approx N \log N - N \quad (64)$$

where the term $(1/2) \log(2\pi N)$ has been discarded as small in comparison to $N \log N - N$. In the homework, you apply Stirling's Approximation (SA) to two-state magnet. Here, we'll apply it to an Einstein solid. Our first approximation is to replace $N - 1$ with N in the original formula for $\Omega(N, n)$.

$$\Omega(N, n) \Rightarrow \frac{(n + N)!}{n! N!}$$

Now apply the SA:

$$\begin{aligned} \log \Omega(N, n) &= \log(N + n)! - \log n! - \log N! \\ &\approx (n + N) \log(n + N) - n \log n - N \log N \end{aligned}$$

Now consider the *high temperature limit*: $n \gg N$. This condition is called the high temperature limit because when $n \gg N$, there are many more accessible energy states than there are QHO's in the solid. In this limit, we have:

$$\begin{aligned} \log(n + N) &= \log \left[n \left(1 + \frac{N}{n} \right) \right] \\ &= \log n + \log \left(1 + \frac{N}{n} \right) \\ &\approx \log n + \frac{N}{n} \end{aligned}$$