

Introductory Thermal Physics v.2.2

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1 Temperature

If the air in the room is heated, we find the speed of the atoms increases. Intuitively, we know to use a thermometer to quantify this phenomenon as an increase in temperature, but if we are going to use a temperature, we should define exactly what it is. There are three different temperature scales you may have heard of: the Fahrenheit, Celsius (also called Centigrade), and Kelvin scales. The names are listed in the order of historical discovery. All are still used, and all are linearly related to one another by simple equations listed below:

$$T(C) = \frac{5}{9}T(F) - 32 \quad (1)$$

$$T(K) = T(C) + 273.15 \quad (2)$$

Equipped with one thermometer calibrated according to each scale, we take careful measurements. We find the average speed squared is proportional to temperature in Kelvin: double the temperature in Kelvin and the average speed squared doubles. The other thermometers yield no such clear correlation. The temperature in Kelvin is referred to as the absolute temperature and this we will define.

Note that room temperature, about 75°F or about 25°C is about 300K.

Examining the atoms carefully, we find the more massive atoms move slower, in fact atoms of twice the mass have half the speed squared. Thus the mass times the average speed squared is a constant, for the heavy as well as the light gases. This product, mv^2 , is exactly twice the kinetic energy, and thus we define absolute temperature as:

The absolute temperature is proportional to the average kinetic energy of atoms in a classical gas.

The one caveat in the statement above is classical. We are discussing physics before 1900, so called classical physics. At low enough or high enough temperature, this definition will not hold.

The constant of proportionality is a key constant of the universe. For us, it relates temperature to average kinetic energy, but we shall find it does far more. It is called Boltzmann's constant and its symbol is k_B and its units are Joules per Kelvin. It is given by: $k_B = 1.38 \times 10^{-23}$ J/K. For historical reasons, there is a factor of 3/2 in the equation:

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}k_B T \quad (3)$$

where the bar denotes average.

1.1 Absolute Zero

At low enough temperature, the above equation suggests that the random motion of atoms would stop altogether. This point, the zero of the Kelvin scale, is known as absolute zero. It is the coldest temperature possible and although it is possible experimentally to get very close to absolute zero, within a thousandth of a Kelvin, absolute zero itself is not attainable. The (good) reason for this is discussed much later.

What does happen near absolute zero? All free energy that can be liberated from an atom has been. There is motion left, due to non-classical physics, and this motion cannot be stopped by further reduction in temperature. In some sense, it is motion without energy. It is beyond the scope of this text.

2 Ideal Gas Approximation

An ideal, or perfect, gas has no collisions with itself, only with the walls of its container, all collisions are perfectly elastic, and it has no rotation or vibration, thus a monatomic gas is typically envisioned. The life of such a gas atom would be spent pinging from one wall to another at constant speed. Using the above equation and solving for average speed, \bar{v} , we find:

$$\bar{v}^2 = 3k_B T / m \quad (4)$$

and in a closed container of volume V , the dimension of which is the cube root of V , collisions will occur once every time t , where t is expressed (using distance is rate times time for constant speed travel) by:

$$t = V^{1/3} / \bar{v}. \quad (5)$$

Such a gas exerts pressure on the walls of the container via these collisions. The force of a single particle of gas would be an erratic function: very large for small times, but then zero as the particle travels to the far side of the container. However, a very large number of particles will create a constant stream of collisions and the pressure will be very nearly unchanging in time. To compute this, we will average the force of the single particle over its travel time between walls, then multiply by the total number of particles to form up the total pressure.

What is the force due to a single particle? The result of the force of the wall on the particle is to change the particle's momentum. The usual expression is $\Sigma \vec{F} = m\vec{a}$ but the right hand side can be rewritten as $\Delta \vec{p} / \Delta t$. The change in momentum during a perfectly elastic collisions is $2mv$ since initially the particle is moving one way with speed v and in the final state it moves the other way with the same speed. Substituting we find:

$$F = 2m\bar{v}/t = 2m\bar{v}^2/V^{1/3} \quad (6)$$

and substituting from Eq. (4) above we find:

$$F = \frac{6mk_BT}{mV^{1/3}}. \quad (7)$$

To total the force, we multiply by N the total number of particles present, but we divide by six because only one sixth will strike any given wall during the time. (We have assumed a cubic container; cubes have six sides.) Further, we want to find the pressure instead of the force. Pressure is force per unit area thus force is pressure times area, and the area of each side of the container is $V^{2/3}$. The total pressure on any given wall of the container is given by:

$$PV^{2/3} = \frac{Nk_BT}{V^{1/3}} \quad (8)$$

Simplifying we find the ideal gas law:

$$PV = Nk_BT. \quad (9)$$

The ideal gas equation is not perfect and we can see the deviations best in graphs. There are two figures, below, which illustrate this.

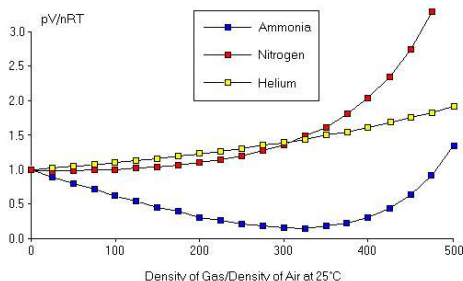


Figure 1: The ratio, PV/nRT , versus gas density for three gases. The y-axis should be one, for all densities. Note that helium is closest to constant, even at high density.

2.1 Definition a Mole

The mole (abbreviated mol) is the number of atoms in 12 grams of Carbon-12¹ This number is 6.022×10^{23} , known as Avogadro Number, N_A , and is vast beyond imagining. Written without scientific notation it is 602200000000000000000000. One mol of house cats would

¹Carbon-12 has six neutrons, six protons - the most common isotope, or “form” of Carbon.

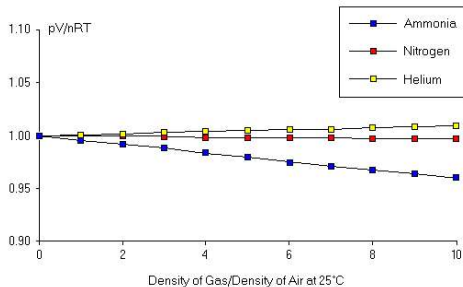


Figure 2: The ratio, PV/nRT , versus gas density for three gases. This is the very low density portion of the figure, above.

correspond to the entire mass of the Earth, converted to felines² - not just coating the surface of the Earth but the entire thing, down to the core, converted to pure *felis silvestris catus*. In terms of money, one mol of dollars has never been spent, nor accumulated. At the present, about 4×10^{13} dollars are spent (exchanged from one hand to another) each year on planet Earth. If our economy had been running since the Earth cooled about \$0.3 mol would have been spent thus far and by the time the Earth is enveloped by the Sun as it turns into a red giant, about \$0.6 mol would have been spent. You have never had a mol of anything that you could hold in your hand (and recognize it was there).

Instead of writing the ideal gas law in terms of the enormous number of particles N , and the tiny Boltzmann constant, k_B , we can rewrite it by multiplying Boltzmann's constant by N_A and dividing the number of particles by the same. The number of particles divided by N_A is the number of mols, n , thus:

$$n = \frac{N}{N_A} \quad (10)$$

and the so-called gas constant R is given by:

$$R = N_A k_B. \quad (11)$$

The gas constant, R , is 8.315 J/(mol K) (Joules per mol-Kelvin). Note one Joule is equal to one Pascal of pressure times one cubic meter of volume, so for pressures in pascals and volumes in cubic meters, this is the constant for you.

However, alternative units abound. Volume is often measured in liters (one liter is a cubic decimeter, or a cube ten centimeters on a side) and pressure often in atmospheres. It turns out that 1000 liters is one cubic meter (10 cubed) and one atmosphere is defined to be 1.013×10^5 Pa, so applying the proper unit conversions, the gas constant R is also 0.0821 L-atm/mol-K.

²Said cats would have to be slightly overweight to account for the entire mass of the Earth. Two mol of standard house cats would be more than sufficient, however.

2.2 Examples of Ideal Gas Law Calculations

Volume of one mole of ideal gas At standard temperature and pressure, we can find the volume of one mole of ideal gas. Standard temperature is zero centigrade, or 273 K and standard pressure is one atmosphere or 1.013×10^5 Pa. Solving for V we find: $V = nRT/P = 1 \times 8.315 \times 273 / 1.013 \times 10^5 \text{ m}^3 = 0.024$ cubic meters of gas, or a sphere of 17.4 centimeters in radius (using $v = \frac{4\pi R^3}{3}$ for a sphere).

Balloon of Ideal Gas A balloon filled with ideal gas has a radius of 5 cm at STP is submerged to a depth 2.2 m under water (density 10^3 kg/m^3). Find the final volume of the balloon assuming the temperature remains unchanged. The extra pressure under a depth of fluid is given by $\rho g d$, where d is the depth under the fluid. This pressure is on top of the one atmosphere of standard pressure. Since n, R, and T are fixed, the ideal gas law can be reduced to: $P_f V_f = P_o V_o$. The final radius is 4.69 cm.

Factors of Two (a) Given an ideal gas, if the volume and temperature are doubled, and the number of mols of gas remains unchanged, find the new pressure in terms of the initial pressure P_o . The pressure is unchanged.

(b) Given an ideal gas, if the volume and pressure are doubled, and the number of mols of gas remains unchanged, find the new temperature in terms of the initial temperature T_o . The new temperature is $4T_o$, since both V and P are doubled.

(c) Given an ideal gas, if the volume, number of mols and temperature are all doubled, find the new pressure in terms of the initial pressure P_o . The new pressure is $2P_o$.

(d) Given an ideal gas, if the pressure is doubled, and the number of mols and volume are both dropped in half, find the new temperature in terms of the initial temperature, T_o . The new temperature is half T_o .

2.3 An Improved Ideal Gas Law: Van der Waal's Equation

In constructing the ideal gas law, several unrealistic approximations had to be made. Principally that particles never interacted with one another (only the sides of the container). This is valid only at low density of particles and with particle species which interact very weakly with one another (such as noble gases).

An improvement was posited by Johannes Van der Waals in 1873 which designates each particle as having a volume b and introduces a parameter a which relates to the strength of interaction between particles. This a parameter resists simple direct physical interpretation. The Van der Waal equation is:

$$(P - a \frac{n^2}{V})(V - bn) = nRT. \quad (12)$$

For Helium gas, $a \approx 0.003 \text{ J m}^3/\text{mol}^2$ and $b \approx 2 \times 10^{-5} \text{ m}^3/\text{mol}$. For Nitrogen gas, $a \approx 0.1$ and $b \approx 5 \times 10^{-5}$ in the same units³. Helium is very weakly interacting thus the very low a

³A table of such parameters can be found at <http://www.ac.wvu.edu/~vawter/Physic-sNet/Topics/Thermal/vdWaalEquatOfState.html> among other places

value compared with Nitrogen, and most other common gases, which have a values on the order of one half (from one tenth to one) in units of $\text{J m}^3/\text{mol}^2$.

Exercise with the Van der Waal Equation Compare the volume of one mole of ideal gas (from above) with the volume of one mol of Van der Waals Helium and Van der Waals Nitrogen at STP.

3 Equipartition Theorem

We defined temperature by using ideal (classical) gases as an example. In doing so, we wrote that: $\frac{3}{2}k_B T = \frac{1}{2}m\bar{v}^2$. The average kinetic energy is three-halves of $k_B T$. In fact, each of the three components of velocity vector have, on average, one half a $k_B T$ of energy.

Energy is equally distributed between these three perpendicular directions. Inherently, this is because we live in a three dimensional world that there are three independent directions and any point in space can be specified by three coordinates and any velocity vector has three rectangular components: the x, y and z components.

Yet what if there were other forms the energy could take, for example potential energy or rotational kinetic energy. How would energy be distributed into these forms?

The answer is the *equipartition theorem*: that an equal amount of energy goes into each possible form of energy, on average, without bias.

Each form of energy is called a *degree of freedom*.

Why should energy be evenly distributed? In a series of elastic collisions, energy will be transferred more frequently from the high energy particle to the lower than the reverse. (The reverse is possible.)

Imagine the extreme case: consider a two dimensional “gas” of frictionless ice hockey pucks initially at rest on the surface of an ice rink. Now shoot two new pucks (from opposite directions to conserve the net zero momentum) at very high speeds into the rink. After many collisions, all pucks will have been struck and thus will have some energy - although it is possible in principle for one to be totally at rest it is essentially impossible.

4 Effect of Temperature on Solids and Liquids: Thermal Expansion

All gases (real and ideal) expand and contract with temperature, as indicated by the ideal gas law. This is a dramatic phenomena. Liquids and solids also expand and contract with temperature, but not nearly so dramatically. Your house (or car or clothes), for example, is not much smaller during winter or larger during summer. Yet we know thermometers - filled, say, with alcohol or mercury - reflect changes in temperature. The marks for various temperatures are nearly linearly spaced on the side. Although it is an approximation, most materials expand linearly in temperature over a small range of temperatures. To formalize this, we need an equation and a coefficient, as follows:

$$L(T) = L_o(1 + \alpha\Delta T). \quad (13)$$

Material	$\alpha \times 10^{-6} 1/^{\circ}\text{C}$
Aluminum	23
Brass	19
Copper	17
Lead	29
Steel	12
Iron	12
Gold	14
Mercury	60
Glass	8.5
Pyrex	3.3
Diamond	1
Quartz, fused	0.59
Silicon	3

Table 1: All numerical values from: “Coefficient of Thermal Expansion”, *Wikipedia: The Free Encyclopedia* http://en.wikipedia.org/wiki/Coefficient_of_thermal_expansion (Accessed 19 April 2017).

where L_o is the length at the initial temperature and ΔT is the change in temperature and α is the coefficient of thermal expansion for a given material. This coefficient subsumes the material dependent properties of the given material: all the microscopic interactions dictating the exact average spacing between nuclei. On average, the atoms grow further apart upon heating - for most materials over most ranges of temperature. Exceptions to this will be discussed below.

Typical coefficients of thermal expansion are small: on the order of $10^{-5} 1/\text{K}$. The unit used is most commonly $1/^{\circ}\text{C}$ or $1/\text{K}$, which are identical since only changes in temperature are considered above, and the change in temperature in Celsius and Kelvin are identical. Some typical coefficients are listed in table 4.

Two long thin metal films affixed together (back to back) with different coefficients of thermal expansion will bend upon a rise or fall in temperature. This so called bimetallic strip has been used traditionally in thermostats to control temperature. A small bulb is affixed to the end of the strip with a conductive liquid (often mercury) and two metal probes. When the temperature increases, the angle of the bulb changes and the liquid will spread over both probes, completing a circuit and allowing current to flow, turning on the air conditioning (or turning off the heating).

5 Thermal Volume Expansion Coefficient

The coefficient of volume expansion, denoted by β , is closely related to the coefficient of linear expansion, α . The formula dictating the volume defines the volume coefficient and is given below.

$$V(T) = V_0(1 + \beta\Delta T) \quad (14)$$

To understand the relation between α and β it is enlightening to consider area expansion. Fundamentally, the understanding of area is the understanding of the factor of two in the derivative of the function x^2 .

5.1 Thermal Area Expansion Coefficient

Consider a square of side length L . Upon a small rise in temperature⁴ there is an increase in length ΔL given by $\alpha\Delta T$. Yet each side is increased by the same ΔL , and thus the total new area is $(L + \Delta L)^2$ which expands in full to:

$$A + \Delta A = L^2 + 2L\Delta L + \Delta L^2. \quad (15)$$

where A is the original area, and ΔA is the increase. Following in the footsteps of equations 13 and 14, we expect the change in area to be given by:

$$\Delta A = \gamma A_0 \Delta T. \quad (16)$$

Identifying the original area with length squared, we find:

$$\Delta A = 2L_0\Delta L + \Delta L^2. \quad (17)$$

Yet by supposition, the change in length is far less than the original length, thus if we can throw away the ΔL^2 term, and using equation 13 to find $\Delta L = \alpha L_0 \Delta T$, we find:

$$\Delta A = 2\alpha A_0. \quad (18)$$

By comparing the above with Eq. 16, we find the area expansion coefficient is (approximately) twice the linear expansion coefficient. The approximation is particularly good when the change in length times length is far less than length squared (e.g. change in length far less than length) yet this condition is necessary to talk about a coefficient at all. None will remain exactly linear over a vast range of temperature. Indeed, upon achieving sufficient temperature, the material will pass through a phase transition and all bets are off.

Similarly, the coefficient of volume expansion, $\beta = 3\alpha$, at least for small changes in volume.

Consider a cube, expanding in all three dimensions. Three faces expand by an amount $\alpha L_0^2 \Delta T$, each face is bordered by two expanding edges, each of which expands by a volume of $\alpha^2 L_0 \Delta T$. Yet three of these edges are shared by two faces, thus there are a total of five such expanding edges. Further, there is one expanding corner which expands by the (assuredly tiny) volume $\alpha^3 \Delta T$. Thus the total volume change is given by:

$$\Delta V = (3\alpha L_0^2 + 5\alpha^2 L_0 + \alpha^3) \Delta T \quad (19)$$

of which we are keeping only the leading term. Thus the volume coefficient is a “worse” approximation than the linear coefficient, and accurate over a smaller range of temperatures (e.g. it becomes a worse approximation more quickly).

⁴In this case, small means such that the extra length is much less than L

5.2 Thermal Expansion Examples

A diamond is held into a gold fitting. Gold has fourteen times greater coefficient of thermal expansion than diamond. What happens as the system is heated? Cooled? How much change in temperature would cause a 0.01 mm change in length if the system is originally 7.5 mm across? Say it begins at room temperature.

Answer: If heated, as the gold expands faster, the diamond will come loose. As cooled, the gold fitting will tighten around the diamond. Perhaps the gold could bend, or break, depending on its material properties.

Now, to get the gold to expand by 0.01 mm, we can compute via $\Delta L = L_O \alpha \Delta T$, and find $\Delta T = \Delta L / (L_O \alpha)$ substituting numbers: $\Delta T = 95^\circ \text{C}$. Which is a very large increase, indeed.

The solution is more complex, since as the gold expands, so does the diamond. This means the actual temperature increase is even larger! To find this, we set the difference in ΔL between gold minus diamond to the 0.01 mm and find $\Delta L_g - \Delta L_d = L_O \Delta T (\alpha_g - \alpha_d)$. So the difference in coefficients of thermal expansion is required. This makes sense since if there is no difference, heating will not help remove one from the other. Numerically, we find: $\Delta T = \Delta L / (L_O \Delta \alpha) = 0.01 \text{ mm} / (7.5 \text{ mm} 13 \times 10^{-6} 1/^\circ \text{C}) = 102^\circ \text{C}$.

6 Physical Underpinnings of Thermal Expansion

Most materials expand when heated. Exotic materials can be found which contract over some ranges of temperature increase. The question why? Solids can be approximated as a set of balls (the atoms) connected by springs (the chemical bonds holding the atoms together). Later we will discuss the exact geometries of bonds and the different lattice types which atoms can be arranged in. Yet true springs expand symmetrically with the application of energy: the energy is proportional to the spring constant and the distance stretched (or compressed) squared. This harmonic potential (proportional to x^2), favors neither expansion nor contraction upon application of more energy - the amplitude of oscillation would increase and nothing else.

Real solids have a more difficult time contracting than they do expanding. At long range, atoms attract one another yet at very short distances they must repel as the electron clouds begin to overlap too greatly. This gives rise to the Leonard-Jones (or 6-12) potential:

$$U(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) \quad (20)$$

as indicated in the figure below. This is the potential energy landscape on which one atom of a solid is allowed to move. At low temperature (low energy) it will reside in the minimum of the valley, and upon heating the temperature rises and the energy is lifted out of the valley and the atom can oscillate back and forth along a line of constant energy. Yet the valley is not symmetric: as the energy rises, the valley opens up more to the left than to the right (e.g. toward larger radius). Every pair of atoms gets further apart upon heating (on average).

Conceptual Question: Imagine a rectangular sheet of metal, with a hole cut in the middle. The sheet is heated to the point where it is now 10% larger in each dimension. Each pair of

metal atoms is that much farther apart. Will the hole expand or contract?

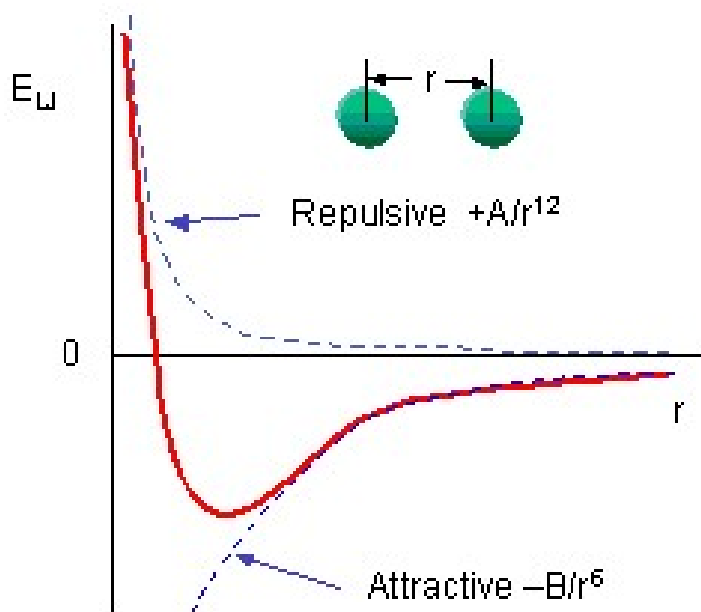


Figure 3: The Leonard-Jones, or 6-12, potential. The y-axis is energy, the x-axis is distance. Near $r = 0$, the energy is very high, and rapidly decreasing, indicating the atoms repel. The energy reaches a minimum, where the atoms are at equilibrium, and as r increases, the energy approaches zero. Why thermal expansion? The energy opens up more to the right than to the left.

7 Statistical Physics

Statistical physics is an extension of classical mechanics to a large number (say, 10^{23} , for example) of particles where complete specification of the position and velocity of each particle is impractical (in the extreme) and has been discovered to be impossible (by the famous uncertainty principles from quantum physics). From the macroscopic, the world of objects on the order of one meter in size, we turn our attention to the world of the atom, on the order of 10^{-10} meters in size. Upon examining the air in a wind-free room, and thus no bulk motion of gas in any direction, we discover each atom is moving - in fact moving very fast. The atoms do not share a single speed, nor a single direction. They collide with the walls and with each other and with everything in the room, giving the air pressure, an omni-directional force per unit area, very nearly exactly uniform throughout.

Thus these atoms have kinetic energy, $\frac{1}{2}mv^2$, and although the mass is quite small, the velocity is high and the energy in, say, a cubic meter of gas is considerable, around 150

million Joules. Momentum is carried by each atom, but momentum is a vector and thus if we sum the total momentum of the (still) air in a room, we must find zero (or a number very close thereto). The air moving left cancels the momentum of the air moving right, same for up and down, same for back and forth. To quantify the situation further, we need to define temperature - despite the disparate velocities and speeds, the gas does have a single temperature, the one your thermometer would read. Not only can we find how the speed increases with temperature, but the exact probability of having a particular speed.

8 Boltzmann's Law of Probability

Given two microscopic states of a system, say, hydrogen gas bonded and separated, what fraction of hydrogen atoms are bonded? A more familiar example may be the odds of the hydrogen - oxygen bond breaking in water generating free hydrogen and O-H. These can be computed via the Boltzmann Equation: the probability of a state is proportional to the Euler's number ($e = 2.713...$) raised to the energy divided by Boltzmann's constant times temperature (in Kelvin):

$$P \propto \exp(-E/(k_B T)) \quad (21)$$

The exponential is called the Boltzmann factor of the state.

8.1 The Two Level System Example

If we consider only two states, A and B , of energies E_A and E_B , respectively, the probability of each occurring is given by:

$$P_A \propto \exp(-E_A/(k_B T))$$

$$P_B \propto \exp(-E_B/(k_B T))$$

Let us called the constant of proportionality C for the moment. The sum of the two absolute probabilities must be one:

$$1 = C \exp(-E_A/(k_B T)) + C \exp(-E_B/(k_B T)).$$

Solving for C we find C is the sum of the Boltzmann factors:

$$C = \frac{1}{\exp(-E_A/k_B T) + \exp(-E_B/k_B T)}$$

In general, C is the sum over all states of the Boltzmann factors:

$$C = \frac{1}{\sum \exp(-E_i/k_B T)}$$

Where the sum is over all states of the system. If there is a very large number of states, this sum is most readily done via computer. The nature of quantum mechanics yields a discrete set of states of various energies. Although a simplistic treatment is either the hydrogens are bonded or they are separate, in reality there is a whole spectrum of states in between.

Thus the probability of a state A is given by:

$$P_A = C \exp(-E_A/(k_B T)) = \frac{\exp(-E_A/(k_B T))}{\sum \exp(-E_i/k_B T)} \quad (22)$$

8.2 Units

Note that all probabilities are unit-less numbers. When multiplied by 100, they are percentages (literally, per one hundred). In and of themselves, they represent the fraction of particles in that state, so 0.5 means half, 0.99 means 99 out of 100, and so on. Probability cannot be negative, nor exceed one.

In joules, energies of single bonds are very small (on the order of 10^{-20} J) thus, for convenience, it is common to refer to bond energies in units of kcal/mol instead of joules (kcal of energy per mol of bonds). Since one mol of particles is $N_A = 6.022 \times 10^{23}$ particles/mol, Boltzmann's constant in units of kcal/mol-K is: $k_B = 1.38 \times 10^{-23}$ J/K = 0.00199kcal/(mol K). Thus near room temperature, $T \approx 300$ K, $k_B T \approx 0.60$ kcal/mol. There are 4.184 Joules in one calorie⁵.

Energies can also be specified in electron-Volts (eV) and this is more common in physics than chemistry or biology. It is the energy an electron gains by moving through one volt of potential difference (the exact nature of a volt is clarified in the second semester of general physics). The unit conversion is: $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$. Thus Boltzmann's constant becomes: $k_B = 8.36 \times 10^{-5} \text{ eV/K}$.

8.3 Arbitrary Zero of Energy

As in previous chapters, the zero of potential energy is arbitrary, and it is useful to set either the highest or lowest energy of the system to zero before computations begin to simplify the algebra. Only differences in energy are real. To see this from a probability standpoint, we can either prove it mathematically or do an example. Here we shall opt for an example.

Consider two states: a and b , with energies 5.55 kcal/mol and 6.55 kcal/mol, respectively, at room temperature, 300K. The difference is 1 kcal/mol. Let us compute the probability of each using the actual numbers and then again setting the energies to zero and one.

Case one: $P_a \propto \exp(-E_a/k_B T) = 9.61 \times 10^{-5}$

$$P_b \propto 1.815 \times 10^{-5}$$

Thus we find our constant, C , is 8752, and the probabilities are:

$$P_a = 0.84$$

and:

$$P_b = 0.16.$$

So state a exists 84% of the time, and state b about 16% of the time.

Case two: In this case, we shall set the lower energy to zero, and the higher (state b) to one kcal/mol. We shall find identical probabilities at the end of the day, but with simpler calculations.

$$P_a \propto \exp(-E_a/k_B T) = \exp(0) = 1$$

⁵Technically, this is called the thermal calorie. There are other subtly different units such as the steam calorie with slightly different conversions, such as 4.182 instead of 4.184. Since they only differ by five parts in then thousand it is not worth exploring the difference unless extreme precision is needed. However there is a similarly named unit, the food Calorie (should be capitalized, often is not) which is equal to 1000 calories, or one kilo-calorie.

$$P_b \propto \exp(-E_b/k_B T) = \exp(-1/0.60) = 0.1889$$

$$C = 0.841$$

$$P_a = 0.84$$

$$P_b = 0.16$$

Which are the same results as in Case one, above.

8.4 Example Computations with Two State Systems

1. At room temperature, one state is twice as likely as the other. Find the difference in energies between states.

We can freely set the energy of one state to zero and thus the energy of the other will be equal to the difference in energies. The ratio of the two probabilities is 2, so we don't have to find C at all. We can simply write down:

$$2 = \frac{\exp(-E_a/k_B T)}{\exp(-E_b/k_B T)}.$$

Setting $E_a = 0$, we find: $2 = 1/\exp(-E_b/0.60) = \exp(E_b/0.60)$. We have used the unique property of exponentials that $\exp(-a) = 1/\exp(a)$, and thus: $1/\exp(-a) = \exp(a)$. Taking the natural log of both sides we find: $\ln(2) = 0.693 = E_b/0.60$ and thus $E_b = 0.416$ kcal/mol.

2. The difference in energies is 1.00 kcal/mol. At what temperature is one state twice as likely as the other?

Again, only the ratio of probabilities is specified, thus we need not compute C explicitly. In this case, energies are specified and temperature is not. We set: $2 = \exp(0)/\exp(-1/0.00199T)$, and thus we see $2 = \exp(1/0.00199T)$. Taking the natural log and solving for T , we find: 725 K.

8.5 Temperature Dependence

In our two level system, the low energy state is always more likely. As T approaches zero Kelvin, the probability of the lower energy state approaches one, that of the higher zero. As T goes to infinity, the two probabilities approach equality. There is no cross over from the dominance of one state to the other which is boring and not at all how real systems work. The probability versus temperature is plotted for a two level system in Fig 1.

9 Entropy and the Boltzmann Law

Consider liquid water and steam. At lower temperatures, water is tightly bound as a liquid. As temperature increases it boils into steam - breaking these bonds and taking on the gas state. The bonds holding the liquid together are energetically favorable even at high temperature, yet they break. Why? The reason is entropy.

Entropy is often said to be the chaos or disorder in the system. In fact, the entropy, S is defined to be: $S = k_B \ln W$, where k_B is the Boltzmann constant and W is the number of available states of the system. So entropy just means there are a number of states. We could enumerate them within the Boltzmann equation, above. This would be painful and long and in many cases unnecessary. Often the system is dominated by clusters of states

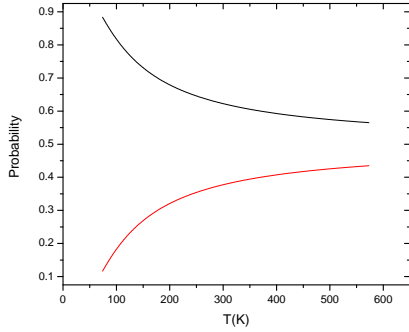


Figure 4: Probability versus temperature (in Kelvin) for a two level system with an energy difference of $2.07 \times 10^{-21}\text{J}$ between the states. The upper (black) curve represents the probability of the low energy state, and the lower (red) curve the high energy state. Note that at low temperature, the probability the system will be in the low energy state goes to unity (and that of the high energy state zero) yet there is a very rapid change in probability at low temperature followed by a very slow change at higher temperature. As the temperature goes to infinity, the probabilities become equal (each is $1/2$).

with similar energies. One cluster we shall call the “bound” state, another the “unbound” state and repeat the two level system with entropy.

Note that entropy has units of energy per unit temperature, the same as Boltzmann’s constant. Although we think of Boltzmann’s constant as a conversion from temperature to thermal energy, it is best *not* to think of entropy this way. Think of entropy as the number of states accessible to the system, multiplied by this funny physical constant, k_B , which happens to have units. High entropy means many states available.

Within the bound state, we sum all the Boltzmann factors: $\exp(-E_0/k_BT) + \exp(-E_1/k_BT) + \exp(-E_2/k_BT) + \dots = W_b \exp(-E_b/k_BT)$, where W_b is the number of bound states, and E_b is the average energy of the bound state. Similarly we find the Boltzmann factor for the unbound state is $W_u \exp(-E_u/k_BT)$. The probability of the bound state is given by:

$$P_b = \frac{W_b \exp(-E_b/k_BT)}{W_b \exp(-E_b/k_BT) + W_u \exp(-E_u/k_BT)}.$$

Yet this complicated expression can be simplified by replacing the W variables with the entropy variables, S . Since $S = k_B \ln W$ by definition, we can solve for W and we find $W = \exp(S/k_B)$. Using the unique property of exponentials that: $\exp(a)\exp(b) = \exp(a+b)$, we find the Boltzmann factor for a state is given by: $W \exp(-E/k_BT) = \exp(S/k_B) \exp(-E/k_BT) = \exp(S/k_B - E/k_BT) = \exp(-(E - ST)/k_BT)$.

The term $E-ST$ is called the free energy, and specifically in this case it is the Gibbs free energy⁶.

Again we can find that the absolute entropy is arbitrary (although, unlike energy, in certain circumstances absolute entropy is computable and can be found experimentally).

⁶Technically, Gibbs free energy is only defined when there is a well defined external pressure on the system and is the sum of three terms: the internal potential energy U , the work done expanding the system: PV , and the entropy term TS , and is written as: $G = U + PV - TS$. In our case, we are lumping the energy U and the PV term into our energy, E and ignoring volume changes.

We can set both the energy and entropy of the bound state to zero and consider only the energy and entropy of the unbound state. In Fig. 2, the probability of each state in a two level system is plotted versus temperature.

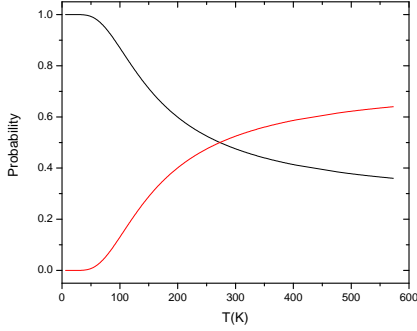


Figure 5: Probability versus temperature (in Kelvin) for a two level system with an energy difference of 4.14×10^{-21} J between the states and an entropy difference of 1.52×10^{-23} J/K. The upper (black) curve represents the probability of the low energy, low entropy state, and the lower (red) curve the high energy, high entropy state. Note that at low temperature, the probability the system will be in the low energy state goes to unity (and that of the high energy state zero) yet there is a very rapid change in probability at low temperature followed by a very slow change at higher temperature. Yet since we are including entropy, the high entropy state (red curve) becomes favored at high temperature. Recall at infinite temperature all states are equally likely and having more states (higher entropy) will thus always be favored. The probability of the high entropy state does not go to unity at infinite temperature, rather to a finite number based on the ratio of the entropies of the two states, in this case 0.75.

9.1 Cases of Two Level Systems with Entropy

The usual case to consider is the bound state of low energy and low entropy (say both zero) and an unbound state with some positive energy and entropy. In this case, the bound state is favorable at low temperature and the system “melts” or has a phase transition, at some temperature T^* , beyond which the unbound state becomes more favorable. It occurs when the Boltzmann factors are equal:

$$\exp(-G_b/k_B T^*) = \exp(-G_u/k_B T^*)$$

which occurs only when the Gibbs free energies are equal. Setting E and S of the bound state to zero, $0 = E_u - S_u T^*$ which means: $T^* = E_u/S_u$.

At this temperature, both the bound and unbound state coexist, with equal probability. In this way, it is akin to the melting temperature of ice (0° C or 273 K) where solid and liquid water coexist. The difference is that at this temperature, any fraction of ice and water could exist: it could be all ice or all liquid water - and there is a macroscopic variable, the heat put into the system (or taken away, in the case of freezing water) which controls this ratio. In the microscopic case of probabilities, both must exist and in exactly equal numbers.

9.2 Examples with Gibbs Free Energy

1. Typical Problem Given two states, the first state with zero energy and entropy, and the higher state with $E = 1$ kcal/mol and $S = 0.005$ kcal/mol-K, find the probability of each at: (a) $T=100$ K, (b) $T=300$ K and (c) $T=600$ K.

The probability of state a is given by: $P_a = \frac{\exp(-G_a/k_B T)}{\exp(-G_a/k_B T) + \exp(-G_b/k_B T)}$, and with $G_a = 0$, this reduces to simply:

$$P_a = \frac{1}{1 + \exp(-G_b/k_B T)}.$$

$$P_a = \frac{1}{1 + \exp(-(E_b/T - S_b)/k_B)}.$$

We know the two probabilities sum to one, thus: $P_b = 1 - P_a$.

In case (a): $P_a = 0.925$

case (b): $P_a = 0.302$

case (c): 0.158

Thus $P_b = 0.075, 0.698$ and 0.842 , in cases (a), (b) and (c) respectively.

From this we can see the gradual crossover from mostly the low energy, low entropy state (a) to state (b). If the energies of the two states are very different, the transition will be sharper. If the system in question is larger this will also sharpen the transition.

2. Disfavored State It is not always the case one state will have both lower energy and entropy. However, if this is not the case, if one state has the lower energy but the higher entropy, this state would always be favored (more than half likely) and the other always disfavored. We shall explore this possibility here.

Consider one state with energy zero, and entropy zero, and another state b , with energy $E=1$ kcal/mol and $S=-0.005$ kcal/mol-K. In this case, state b will always be disfavored, but the question is by how much? Compute the probability of each state occurring at: (a) $T=150$ K, (b) $T = 300$ K and (c) $T = 450$ K.

The probability of state a is given by:

$$P_a = \frac{1}{1 + \exp(-(E_b/T - S_b)/k_B)}.$$

But in this case the numbers differ slightly and S_b is negative. Solving we find:

$P_a = 0.997, 0.985, 0.974$ in these three cases. Thus the state b is slightly more favorable at slightly higher temperatures, but the system is always more favorable to state a .

We can take the limit of very high (infinite) temperature and in this limit:

$$P_a = \frac{1}{1 + \exp(S_b/k_B)}$$

Which in this case is: 0.925 .

The Inverse Problem: In General In general, we can set the energy and entropy of one state to zero, thus the Gibbs free energy of that state is always zero ($G = E - TS = 0 - T0 = 0$). And we shall call the Gibbs free energy of the other state ΔG since it is the difference in free energy between the two states:

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

Where: $\Delta E = E_b - E_a$ is the difference of the energy of state b minus that of state a , and the same for the entropy: $\Delta S = S_b - S_a$ and with these definitions we find:

$$P_b = \frac{1}{1 + \exp(-\Delta G/k_B T)}$$

This we can easily rearrange and use to solve for $\Delta G/k_B T$ in terms of the probability. This is useful if the probability is given and something is desired. Rearranging we find:

$$\exp(-\Delta G/k_B T) = \frac{1}{P_b} - 1.$$

Taking the natural log of each side we find:

$$-\Delta G/k_B T = \ln(\frac{1}{P_b} - 1).$$

3. An Example of the Inverse Problem Consider a two level system with state b having 5 kcal/mol more energy than state a and state b having 1.5 kcal/mol-K more entropy. At what temperature will the two be equally likely?

We compute ΔG and set the probability to one half to find:

$$-(5 - 1.5/k_B T)/k_B T = 0.$$

Distributing the denominator of the right hand side we find:

$$-(5/k_B T - 1.5) = 0.$$

And thus we see:

$$-5/k_B T = -1.5$$

or:

$$5 = 1.5 k_B T$$

recalling: $k_B = 0.00199 \text{ kcal/mol-K}$, we find:

$$T = 1675 \text{ K}.$$

This is a pretty stable bound state. The lower energy and entropy state, state a, will be dominant until 1675 K, at which point state b takes over.

4. Finding an Entropy Difference At 300 K, one state is 4.5 kcal/mol of energy more stable than the other, and 80% of all particles are in this low energy state (state a) (at 300 K). Find the difference in entropy between states.

We know $P_a = 0.80$ and thus $P_b = 0.20$ at 300 K, so we can use our inverse equation from above:

$$-\Delta G/k_B T = \ln(\frac{1}{P_b} - 1).$$

And solve for the free energy change ΔG , first:

$$-\Delta G/(0.6) = \ln(5 - 1) = 1.386.$$

Solving for ΔG , we find:

$$\Delta G = -0.832 = \Delta E - T\Delta S.$$

Now inserting the given $\Delta E = 4.5$, we find:

$$\Delta S = 0.0178 \text{ kcal/mol-K}.$$

9.3 Units of Entropy

The SI unit of entropy is the Joule per Kelvin (J/K). For convenience, we have used kcal/(mol-K) in this work. However, there is another unit of entropy commonly used in the literature called simply the entropy unit, oft abbreviated e.u. It turns out the “entropy unit” is defined as one calorie per mol-K. Not the kcal, just the calorie. This is a convenient unit because typical bonds have entropies on the order of one e.u.⁷

⁷At first glance, this may seem odd that the entropy values are measured in cal/(mol-K) while the energies are measured in kcal/mol - but recall that room temperature is around 300 K and the Gibb's free energy

9.4 Finding Average Values via Derivatives of the Partition Function

Above, we discuss how to find probabilities of individual states. How does this relate to experiments? Average values can be easily computed from the partition function, Z , above. These averages can be related directly to experiments.

Normally, when taking an average, we sum the things, and divide by the number. For example, if we were to find the average test score, we sum all test scores, and divide by the number. In the language of probabilities. This is most easily seen by example.

Consider seven quiz scores: 7,8,8,8,9,9,10. Now the average is $(7+8+8+8+9+9+10)/7 =$ about 8.43. This is like saying each quiz paper is equally likely, occurring one time in seven⁸. This is equal to saying a score of 7 occurs once in seven times, a score of 8 occurs three times in seven, and so on. So we re-compute the average as: $(7+3 \times 8+2 \times 9+10)/7$. In general, the average is the probability of the score times the score, summed over all scores.

$$\bar{x} = \sum P_{xi} \times x_i$$

As we have already found the probabilities, above, then it can be easy to find average values.

Consider average energy, \bar{E} . For two state system: $\bar{E} = P_a E_a + P_b E_b$. Since $P_a = \exp(-E_a/k_B T)/Z$, we observe the energy is stored within the Boltzman factor, just waiting to be moved down, in front, by taking the appropriate derivative. At first, you may consider taking a derivative with respect to temperature, T , but in fact, a derivative with respect to one over temperature is required. To clean up the notation,

$$\text{let } \beta = \frac{1}{k_B T}.$$

$$\text{With this we see: } \bar{E} = -\frac{1}{Z} \frac{d}{d\beta} Z.$$

Many other average values can be obtained by taking appropriate derivatives. Among these are the: specific heat, compressability, magnetization, polarization, chemical potential, and reaction rates.

Paramagnetism An example of a two state system is a paramagnetism of isolated electrons. Now, the electrons are bound to atoms in some large crystal, but most electrons are paired with a friend, and their spins cancel. Certain crystals with complex structure have, periodically, an atom with one unpaired electron. This one is magnetically isolated, and interacts only with an external field, B applied. Such an electron has two states: spin up and spin down. One aligns with the field, one counter-aligns with the field. We term aligning spin up, and since this is favorable, it has negative energy. These are linearly related to the field by the constant μ_B , the Bohr magneton, which we will simply write μ for this section.

The energies are $+\mu B$ and $-\mu B$, so the partition function, Z is given by:

$$Z = \exp(\beta \mu B) + \exp(-\beta \mu B).$$

We are using $\beta = \frac{1}{k_B T}$ to simplify the exponents. You may recognize this sum of exponents as the hyperbolic cosine, \cosh , which is defined as $\cosh x = e^x + e^{-x}$.

contribution of entropy is temperature times entropy - so it makes sense to have a “smaller” unit of entropy since it is multiplied by a large number.

⁸This sounds like the scores are random and each student has a one in seven chance of scoring 10, but whether the score is random (drunk grading by the professor, perhaps) or due to the efforts of the students (hopefully) we can take the average either way.

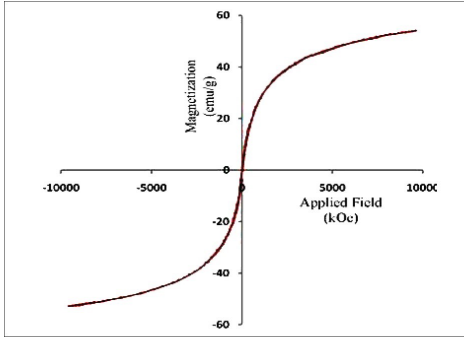


Figure 6: Magnetization, M , versus applied field, B , for superparamagnetic iron-oxide nanoparticles (SPION) which may, someday, be used to deliver drugs to targeted areas. Superparamagnets are, effectively, just unusually powerful paramagnets. In this case, they are using materials which normally would be ferromagnetic, but making tiny (nanoparticle sized) versions of them: in which case, the ferromagnetism cannot take over, and they are left behaving as very strong paramagnets. The units of the graph are not our normal SI units.

The probability of finding a spin up is given by: $P_{up} = \frac{\exp(\beta\mu B)}{Z}$. Note the two minus signs cancel in the exponent: one from the Boltzmann factor, and one from the energy being negative for spin up. Similarly, the probability for spin down is: $P_{down} = \frac{\exp(-\beta\mu B)}{Z}$.

The magnetization of the sample is μ times the difference in the number of spins up and spins down. To get the total number of spins pointing up, we multiply the probability by N , the total number of unpaired electrons (spins) in the system.

$$M = N\mu(P_{up} - P_{down})$$

Substituting the probabilities found above we find:

$$M = N\mu(\exp(\beta\mu B) - \exp(-\beta\mu B))/Z.$$

This difference in exponents is the hyperbolic sine, \sinh , given by: $\sinh x = e^x - e^{-x}$, and \sinh divided by \cosh is \tanh , so it simplifies to:

$$M = N\mu \sinh(\beta\mu B) / \cosh(\beta\mu B) = N\mu \tanh(\beta\mu B).$$

In the figure 6, we see the resulting magnetization plotted versus applied field. The shape of the curve is a hyperbolic tangent.