Calculating Energy

Energy is a rather nebulous term. We need to be very clear in the definition. For example, a particle of mass m may have potential energy if it is in a gravitational field, or it can have energy if the mass is directly converted to energy, as Einstein's famous formula shows. For chemists we are interested in the potential energy associated with molecules being attracted or repelled from one another, or in chemical reactions where old bonds are broken and new ones are formed. We are also interested in the kinetic energy that molecules have. We are really thinking of molecules as nearly classical objects, and putting aside for now the quantum mechanics that makes molecules what they are. Whatever the origin of the energy, we are really only interested in the energy involved in a change, and therefore we must be clear about the process (chemical or physical) that molecules undergo.

The simplest example of energy is the kinetic energy of a molecule such as O_2 or N_2 as the two most important gasses in the air we breathe.

How much kinetic energy does an O_2 molecule have? (This is not an energy change but energy due to motion.)

An O_2 molecule (in the air @ Room Temperature) is moving about 400 m/sec. (as an rms speed). The energy (of a single molecule) then is:

$$\varepsilon = \tfrac{1}{2} mv^2 = \tfrac{1}{2} \frac{32 \cdot 10^{-3}}{N_A} (400)^2 \frac{kg - m^2 / \sec^2}{molecule} = 4.3 \cdot 10^{-21} \, J / molecule$$

$$E = \varepsilon N_A = 2.6 kJ / mole$$

This calculation teaches many things. Not only did we use the formula for energy, we practiced going between the energy of a single molecule and that of a mole of molecules, noticing that the energy scales linearly with number of molecules, and we use the SI (or mks) system of units.

In addition to kinetic energy, there is potential energy. There is also chemical energy, which is much like potential energy in that it represents energy stored in a molecule. An example of chemical energy is to find:
How much energy is in an 8 oz cup of yogurt (226 grams)? (You may look at a yogurt cup for the relevant information.)

The conversion for carbohydrates is 4 C/gm, and there are 37g of sugar. Talk about mixed units. C is a big calorie which is 1 kcal, and 1 cal = 4.18 Joules. So we can get the number of Calories: $37 \bullet 4 = 150$ Cal$= 1.5 \cdot 10^5 cal = 6.3 \cdot 10^5 J = 630 kJ$

This calculation shows how one uses ordinary events in the environment to estimate energies of objects. In the first case it is the motion of molecules, in the second case it is the energy of conversion from a carbohydrate to carbon dioxide and water (you burn the yogurt). So process is very important.

How is work connected to energy? If you put work into a system, then the system will increase in energy. So let's think about moving an object, of mass m. The environment (i.e. you) must apply a force, F, on the object and actually move it in order to do work on the object. The work moves the object and so the object gains speed, and hence kinetic energy. Mathematically then:

$$w = F \cdot l$$
$$\delta w = F \cdot dl$$
$$w = \int_a^b F \cdot dl$$

The work that you do (or put into the system) must increase the energy of the system, ΔE, so $\Delta E > 0$ in this case.

Prove that the work put in increases the energy of the system:

Newton's law states that the force I apply changes the momentum (or velocity) of a particle by some amount, i.e. causes some sort of acceleration: $F = \frac{dp}{dt}$, where the momentum $p = mv$ and the velocity is $v = \frac{dx}{dt} = \frac{dl}{dt}$. This sort of equation is not a simple definition of force. It equates something I do with something that happens to the object I am pushing on. The new relation we seek contains this same character. We will show that $\Delta E = w$. This is not a trivial statement; it connects what I do (work) with what happens to the object (it gains energy.) The object is moved from position a at time t(a) with velocity v(a) and ends up at position b at time t(b) with velocity v(b).

From the definition of a force:

$$w = \int_a^b F \cdot dl = w = \int_a^b m \frac{dv}{dt} \cdot dx = m \int_{t(a)}^{t(b)} \frac{dx}{dt} \cdot \frac{dv}{dt} dt$$
$$= m \int_{t(a)}^{t(b)} v \cdot \frac{dv}{dt} dt = m \int_{v(a)}^{v(b)} v \cdot dv = \tfrac{1}{2} m v^2 \Big|_{v(a)}^{v(b)} = E \Big|_{v(a)}^{v(b)}$$
$$= E(b) - E(a) = \Delta E$$

The definition of force and velocity in terms of particle dynamics were used to show that work becomes energy (of the system, or particle in this case). This is very close to the first law of thermodynamics. This equation might be called the first law of dynamics (although I just made that up). The first law of thermodynamics is that not just work, but work and heat can be used to increase the energy of a system. (Much more about that later.)

How is the energy of a gas in a box related to the usual quantities that define the gas in a box: mainly volume of the box, number of gas molecules in the box; weight of the gas molecules of the box; the pressure exerted by the gas molecules on the wall of the box; and finally the temperature of the box? We will study the gas in a box for at least three weeks; believe it or not there really is that much to say about a very mundane system. But if you really want to get an understanding of tires and engines, and how energy is used in our environment, you can't begin at a better place.

Let's now consider an example of potential energy, in the earth's gravitational field. How much energy does it take to lift a weight (mass)?

A person bench pressing 100 kg (which is about 220 pounds) pushing the weight about 1 meter (3 feet). How much energy does that take? We use our above connection: We can compute the force and we know the distance so we can compute the energy of the weight that was lifted. In this case the energy stored in the weight is not kinetic energy at the end but it is potential energy. When one is done lifting the weight is not still moving because the kinetic energy put in by the weight lifter was converted to potential energy by the earth's gravitational field. If you lifted the weight in space (no gravity) you would have imparted the same energy but there the weight would keep going, as the imparted energy would be kinetic. So, what is the force you impart? The weight lifter (you) imparts just enough to compensate for gravity so the force of gravity is $F_g = mg$ where $g = 9.8m/\sec^2$ (on the earth). The work done is related to the energy difference (now potential energy) as: $\Delta E = w = F_g h = mgh$ where h is the height of the lift, $h = \Delta x$. In this case the mass is 100 kg and the mass is lifted 1m. So the work is $\Delta E = w = mgh = 100 \cdot 9.8 \cdot 1J = 0.98kJ \sim 1kJ$. Therefore the raising of the weight, which is more than I can lift, is one kJ of energy. Not very much energy when you look at what you get from a cup of yogurt, which is 630 kJ. You would have to bench press for an hour or so, if possible, to utilize the energy in the yogurt cup. (For us in a food rich society, the good news is that we convert the yogurt energy to work at about 60% efficiency so you really only get about 400kJ from your yogurt. Much more about this later.)

So hopefully we have an idea of the connection between energy in our food and energy used by us when we work (or play). The different forms of energy are very important, we have given examples of both kinetic and potential energy, as well as chemical energy; but it is all energy.

Now back to the gas in a box: How much force does a particle exert on a wall if you have it inside a box?
To begin: Imagine a box that has dimensions Lx, Ly by Lz. The lhs of the box is at the origin. At the position x=Lx, there is a wall of area A=LyLz. That wall can be moved to the right or left. When it is moved to the left the volume of the box decreases and the external force (the one pushing the wall) does work on the gas in the box. As we will see the velocity of the gas increases because of the work. Let's now consider a single particle moving with velocity v just along x, v_x, in the box. The particle hits the wall of interest (at x=Lx) and elastically bounces off so that it now goes back to the other wall, bounces off it and comes back. The time to travel down and back is Δt and it is connected to the other quantities: $v_x = \frac{2L_x}{\Delta t}$. The energy of the particle is only in the x

direction: $\varepsilon_x = \frac{1}{2}mv_x^2$. You must provide a force on the wall to just balance the force of the particle pushing on the wall. No work is being done to maintain the box because the wall is not moving. Remember work requires something to move, not just pushing with nothing yielding. So the force the wall exerts on the particle is equivalent (by Newton's law) to the change in the momentum of the particle upon striking the wall divided by the time of each strike: $F = \frac{dp}{dt} = m\frac{\Delta v}{\Delta t} = m\frac{(-v)-(+v)}{\Delta t} = -2m\frac{v_x}{\Delta t}$. Using the above definition of the time:

$F = -2m\frac{v_x \cdot v_x}{2L_x}$. The negative sign shows that the external force (from the wall) causes the particle to move in the –x direction, which is what you expect. After all, the force is the force the wall exerts to keep the particle in the box. Because the forces balance, nothing moves. Now, if I want to actually compress the gas, I must push a little bit harder on the wall than the particle does to push the wall out. (I could go the other way and yield to the particle in the box and let the particle push the wall out, we will consider that case later; but you can guess that the results are just about the same because of the reciprocal nature of pushing and yielding.) So now let's do a little bit of work and move the wall in: $\Delta E = \Delta\varepsilon_x = w = F\Delta L$. The energy of the particle must change as the wall changes, or $\frac{\Delta\varepsilon_x}{\Delta L} = F \geq -m\frac{v_x^2}{L_x} = -2\frac{\varepsilon_x}{L_x}$. The minus sign might seem surprising, the energy E and length of the box are always positive, but if I push in on the box just enough to overcome the force of the particle then ΔL will be negative and ΔE must be positive. Therefore, when the box gets smaller the energy of the particle goes up. Therefore, the force the particle exerts of the wall in the x direction is: $F = 2\frac{\varepsilon_x}{L_x}$. Notice the sign switch, as this is not a change in either the energy of the particle or the length of the box.

Lets summarize this case: I did work; I pushed with a force just large enough to overcome the force of the particle and cause the box to contract. Therefore the energy (as kinetic energy) of the particle must go up to balance the work-energy relation. This is the reason for the slight inequality, because my force is taken to be just a tad bit more than the force of the particle. The forces must not exactly cancel, because then no work is done, and the walls of the box do not move.

Now let the particle move in any of the three directions and the energy is: $\varepsilon = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right)$. On average the velocities and hence the energy will be the same in each of the three directions. The force times the length then will be the same on average also: $\bar{\varepsilon} = \frac{1}{2}m\overline{v^2} = 3\bar{\varepsilon}_x$, If we now work in units of moles of independent gas molecules in the box, we can multiply the mass and the energies by Avagadro's number and let:

$E = N_A\bar{\varepsilon} = \frac{1}{2}(N_A m)\overline{v^2} = 3E_x$, and we let the average force in the x direction be:

$$\bar{F}_x = 2\frac{E_x}{L_x}$$

Because $\bar{F}$ is the average force the wall exerts on the particle then the force of the particles is just the same and of opposite sign, therefore:

$\frac{1}{3}E = \frac{1}{2}\bar{F}_x L_x$. We can multiply and divide by the area of the wall, $A_x = L_y L_z$, to bring in the idea of pressure that the particle experts: The pressure is $P = \frac{\bar{F}_x}{A_x}$, and again we would expect the pressure on each face to be the same for each wall, if we averaged over many hits: $\frac{1}{3}E = \frac{1}{2}\bar{F}L_x = \frac{1}{2}\frac{\bar{F}}{A_x}(A_x L_x) = \frac{1}{2}PV$. The volume of the box is $V = L_x A_x = L_x L_y L_z$. Therefore, one does not need a different pressure gauge on different faces of the box, the pressure, on average, is the same all around. When a single particle hits a wall the force must be distributed over the entire wall because the wall must move as a unit. Therefore, the larger the area the more probable the hits are so that the force per area would be a quantity that is independent of the size or area (or shape) of the container. The forces on larger walls are larger but the forces divided by the area (pressure) are the same. One can use the idea that the particle energy should be the same regardless of direction (on average) to reason that pressure is independent of the size or shape of the container. This is a more universal way to understand forces as it takes into account the proper averages over many particles moving randomly.

Work and Pressure:

We can now go back to our equations for work and energy and use the new ideas of volume and pressure to realize that:

$$\Delta E = w = F\Delta L = \frac{F}{A}(A\Delta L) = -P_{ext}\Delta V$$

The minus sign is there, in accordance with our convention above, because if the box expands then the box does work the volume increases, $\Delta V > 0$, and the energy of the gas must drop because the gas did work. The external pressure is the pressure on the yielding side and must be less than the pressure of the gas inside the box ($P_{ext} < P$). Above we did the example that the gas energy increased because $\Delta L < 0$ hence $\Delta V < 0$. When the gas does work on the environment we say that work moved from the gas (or system) to the environment. When we do work on the system the work is positive, work energy was put into the system, and the internal energy of the gas goes up (increases).

How about a quantum mechanical particle? In chem. 455 you solved for the energy of a quantum mechanical particle in a box. The kinetic energy of a free particle is the same whether it is quantum mechanical or classical. We use the deBroglie relation between the wave vector, k, and the momentum, p:

$$E_q = \frac{1}{2}mv^2 = \frac{1}{2m}p^2 = \frac{1}{2m}(\hbar k)^2$$

The particle in a box has the solution that the wave function goes as $\sin(kx)$ and must vanish at the wall of the box, where $x = 0$ and $x = L$. This constrains the wave vector to certain quantized amounts proportional to a positive integer, n: $kL = \pi n$, where the sin function is zero at both walls of the box. Therefore the energy depends on the length of the box:

$$E_q = \tfrac{1}{2}mv^2 = \tfrac{1}{2m}p^2 = \tfrac{1}{2m}\left(\frac{\pi n\hbar}{L}\right)^2$$

The finding about the classical particle is that: $\frac{dE}{dL} = -2\frac{E}{L}$. The amazing thing is that this is true for the quantum mechanical particle as well. Therefore, if we push the wall in, slowly so that the quantum level is not changed (n stays constant), the energy of the particle will increase as though the particle were classical. From the outside of the box you cannot tell if the particle is a quantum mechanical one or a classical one.

Now let's apply what we know about a gas in a box to determine what happens when we compress a gas. Suppose the gas is an ideal gas (I.G.) and PV=nRT. Let's start with 1 mole of a gas at Thermodynamic standard conditions. This is 1 Atm and 25C. For the SI system we need to convert to SI units. There is a slight difference between an Atm and a Bar, which shows up in the different values of the gas constant. The bar is $10^5 Pascals$, which seems like a large number (it is!!!).

How big is the box holding n=1 mole of the gas when the box is a simple cube?
Using the I.G. equation of state and R in SI units, and $V = L^3$, we get

$$L^3 = V = \frac{nRT}{P} = \frac{1 \cdot 0.082 \cdot 298}{1}\ell = 24.436dm^3 = 0.024m^3$$

$$L = 0.3m$$

So to check our results: From Avagadros principle a mole of gas should occupy 22.4 l. This is about 11 - 2 liter. bottles of soda. If you arrange 9 bottles in a square you get the approximate volume of space needed because the bottles occupy about 70% of the space. So a box that holds 9 two-liter bottles of soda would be about the right amount of space for a mole of gas. And that is about 1 foot on a side. The calculation gave 1/3 of a meter which is about a foot.

So we have a gas in a box at one atmosphere of pressure. Let's imagine that the top of the box is movable (like a piston in a car engine). How much weight do we have to put on top of the box to get the gas to compress to ½ of its volume (at the same temperature)? (We will later do the harder case, where the gas does not come to equilibrium with the environment.)

I think the answer is quite surprising. I would have thought that if I stood on the box (with my 170 pounds, 77kg) that it would have pretty much compressed the box. Well, I guess I should pay more attention to what happens to tires when I get in a car (Nothing!!!).

So let's do this problem the way we know from Thermodynamics and what we have from above. The gas in the box stays at the same temperature (it is isothermal). We do work on the box, the extra force of an additional atmosphere is needed to compress the gas. We know this because at the start $P_0V_0 = nRT = P_1V_1$ at the end. The volume is reduced by a factor of 2 so the pressure must be doubled. The compression did work on the gas, the gas compressed and the energy of the gas went up, as the gas increased its kinetic energy. However now we let the gas cool by coming back to the original temperature. The cooling means that heat goes out of the box and into the surroundings or the environment.

We must put a weight of some mass on top of the box to compress the gas. The final pressure is 2 Atm. What is the weight that is added to the 1 Atm of pressure already present on the box (from the air in the environment)?
Answer: We need a pressure of 1 atm distributed over a surface that is a square 0.3m on a side. Pressure is force per unit area, (we have the area) and the force is the mass times the gravitational constant. Therefore: $P = 1Atm = \frac{F}{A} = \frac{mg}{A}$. Let's work in the SI system. $1Atm = 1.01 \cdot 10^5 Pa$. $A = 0.3^2 m^2$, and $g = 9.8 m/\sec^2$. Substituting all this in gives the answer in kg. $m = \frac{AP}{g} = \frac{0.3^2 \cdot 1.01 \cdot 10^5}{9.8} kg = 0.92 \cdot 10^3 kg \sim 1kT$. I did all the numbers but one should look at the answer. It takes a kilo-ton to compress a gas in a box to half the volume. A kilo ton is just about the same as a ton in pounds, it is 2.2-thousand pounds. This strikes me as quite large. Is this reasonable? Well, what gave us the 1 Atm pressure in the first place? A column of air about 60 miles high. That ought to weigh something. We know that the barometer is a column of mercury 760 mm high. This is 1 Atm, 760 torr.
If we build a box that is 0.3m by 0.3m on the bottom and 0.76m high and fill it with mercury this should be what it takes to generate a pressure on this top. The density of mercury is 13.4 gm/cc or in SI units: $13,400 kg/m^3$. The mass of such a volume of mercury then is: $(0.30 \cdot .30 \cdot .76) m^3 13,400 kg/m^3 = 0.96 \cdot 10^3 kg$, so yes it does just about agree (there has been a little rounding here and there), and boy that is a lot of mercury.

The forces involved in compressing a gas are quite remarkably large, by a human standard. So, as a practice, how much would a human compress the box by standing on it?

Even with these large forces, one should realize that the atoms of the gas take up about 1/1000 the space allotted to them. You can get this estimate quickly by noting that water is 1 grams/cc and that air is 1 gram/liter; here the cc and the liter are 1000 times different. If you don't think too hard about the difference between an air and a water molecule (28 vs 18 g/mole) and assume that a water molecule and air molecule take up about the same amount of space you get this factor of 1000. So there is lots of room to pack more air molecules together, but it is going to take a lot of work.

So how much work would we do on the gas if we compressed it by a factor of 2?

$$w = Fdl = mgh = \left(1 \cdot 10^{3} kg\right)\left(9.8 m/\sec^{2}\right)\frac{0.3}{2} m$$

$$= 1.47 kJ$$

Notice that this work is about the same as it was to lift a 100kg weight (about 1/10 the weight of what is needed here) but to move it 1 meter (about 5 times the distance moved here). Again compared to that yogurt cup, you have plenty of energy from the yogurt to compress this gas or lift a weight. Developing the machine required to do the lifting, converting the energy in the yogurt to work could be pretty challenging however.