Chapter 18 ENERGY, Part 1

We continue assembling the pieces of the Grand Puzzle, but we now move to a different portion of the Puzzle. We are going to start on that part which deals with energy. Energy is very important to your life and to the universe as a whole. All of chemistry, all of biology, all of physics, etc. are determined by energy and changes in energy. This is a very simple and very important notion.

18.1 Economics

Energy is the economics of Nature. It makes things possible, although it doesn't necessarily make them happen. Energy is a capability to do something. It's like money. Money is the capability to buy and to do. (Sorry, Nature does not issue credit. You must have the energy at time of purchase.) Energy and money are <u>capabilities</u>. Having them means that things are possible, but it does not mean that those things will happen. You must understand this. If you have the money to buy the tablet, it does not mean that you <u>will</u> buy the tablet. You might save the money instead. Likewise, having energy means something <u>can</u> happen, but it does not necessarily mean that it <u>will</u> happen. If not used, the energy is saved (stored). Consider a can of gasoline which also has air inside it: this mixture of gasoline and air has the energy (capability) to blow up, but this doesn't happen by itself. There are actually two parts to this picture: whether something <u>can happen</u> and whether something <u>will happen</u>. These two parts will take some time to develop. We discuss only one aspect of <u>can happen</u> in this Chapter and into the next; we will postpone the remaining aspects until Chapter 44. The part of the picture dealing with <u>will happen</u> will start in Chapter 48.

I want you to remember the economics stuff. It's a very easy connection to make. It's a very important connection to make. Let's say you have some amount of money. I don't care how it's stored, such as in savings or in checking or in cash or in a mattress. We'll consider that money to be your cash assets. (As used herein, "assets" will be defined for cash or available cash, not for goods.) When you work, you receive money and your assets increase. When you do something like make a purchase, or go out to eat, or skateboard the Himalayas, you pay and your assets decrease. These are transactions. These are cash flows. They can occur in either of two directions: you can gain money or you can lose money. Your assets can go up or your assets can go down. For any transaction, you begin with some amount of assets and you end with some amount of assets, and the difference is the transaction amount or cash flow. It does not matter if you paid off a purchase in one single payoff or if you paid in three monthly installments. It does not matter if you dealt in paper bills, coins, checks or whatever. The only really important factors are what you start with, what you end with, and the transaction amount. These three are related arithmetically. We can write this as

$$\text{transaction amount} = \text{final assets} - \text{initial assets}$$

If you understand this much, you are in excellent position to understand the role of energy in your world. As applied to energy, this is the same relationship for every reaction in every cell in your body. Energy is Nature's economics. This is the basis for everything that you ever do in your life.

18.2 Joule

Money comes in different forms involving different currencies in different countries, and even different denominations within any one country. Energy also comes in different forms and we are exposed to numerous forms of energy on a daily basis. Heat is associated with hot or warm things but cold things also have heat energy; cold things simply don't have as much thermal energy as when they're warm or hot. This was mentioned in Chapter 1 when we talked about absolute zero. Every temperature above absolute zero represents some amount of thermal energy. Even a block of dry ice at −78 °C (−108 °F) has some heat energy. There's also light or radiant energy, which is the energy associated with electromagnetic radiation. This includes light that you see but also light that you cannot see. For example, anytime you stand near a fire, such as a fireplace or a campfire, you can feel the glow even with your eyes closed; that's also radiant energy. Mechanical energy includes the energy of common forms of work such as done by various engines. Chemical energy is another form of energy; it is chemical energy that powers everything you do. Another common form of energy is electrical, which is associated with pushing/pulling a bunch of electrons through some device. A final form of energy to note is nuclear, especially the natural kind. The Sun is a nuclear fireball, a nuclear furnace of incredible magnitude. Even the Earth has its own nuke stuff going on within. It's nowhere near the magnitude of the Sun, but it does add heat to the planet.

All forms of energy are interconvertible. Just like currencies. Energy is energy, whether it's thermal, radiant, mechanical, chemical, electrical or nuclear. Let me show a simple illustration. It starts 93,000,000 miles away, give or take a twain or two. The Sun does its nuke thing, converting nuclear energy into huge, unfathomable amounts of energy. This energy takes many different forms such as heat, light, the high energy particles of the solar wind, etc. After a short trip of fifty seconds at the speed of light, a minuscule fraction of the radiant energy strikes half of Earth. That light energy can then undergo more conversions. For example, much is converted to heat; this is clearly evident by walking barefoot across asphalt on a sunny summer day. The heat energy contributes to weather. The winds of weather can then be tapped for mechanical energy which can be used directly or which can be converted into electrical energy. The Sun's radiant energy can also be converted to electrical energy using solar cells. Crucial to life on Earth, some of the Sun's radiant energy is absorbed by plants, which are the true workhorses of the planet. That beam of light smacks into that chlorophyll or other absorber molecule, and this starts the photosynthetic conversion of radiant energy into the chemical energy of sugars. Almost every critter on this planet depends on photosynthesis for life, including you. Once a plant converts solar energy into chemical energy, then bugs and higher animals might eat the plant, thus acquiring that chemical energy. The chemical energy now provides the animal with energy for heat and for work. The food chain continues to the next critter and the next critter and so forth, transferring chemical energy at each step. Humans eat plants and animals, which continues the transfer of chemical energy along the food chain. Now remember where it all began: in essence, those Calories of energy can be traced back to the Sun's nuclear reaction 93,000,000 miles away. In essence, you are powered by an alien energy source. But don't tell the tabloids or they'll try to make headlines out of it.

At a fundamental level, energy and mass are mutually interconnected, and this connection is called mass-energy equivalence. Energy has some amount of mass and mass has some amount of energy. The grand total of mass-energy stays the same across the universe; this constitutes the law of conservation of mass-energy. But energy has only a minute amount of mass, so you need to have a humongous amount of energy in order to have a measurable amount of mass. Humongous amounts of energy are involved in nuclear processes, and we will apply the mass-energy relationship to those in Chapter 68. On the other hand, chemical reactions, even explosions, do not involve such humongous amounts of energy; because of this, the mass of the energy involved in chemical reactions is ridiculously small and not significant. This has been the basis for our coverage so far for conservation of mass, as reflected in the conservation of atoms and the conservation of matter. Now we will be adding the conservation of energy. Conservation laws are extremely important and are some of Nature's most fundamental laws. You cannot violate them, although many have tried.

We need to do some units somewhere in here. Now looks like a good time.

There are not many units of energy which are commonly encountered. The nutritional Calorie is probably one of the most common. Another is BTU, which you might hear about when buying a room air conditioner or such. Other than that, energy units are not a common item of conversation. I introduced the SI unit of energy in the last Chapter. It's the joule, J.

$$\mathrm{J} = \frac{\mathrm{kg} \bullet \mathrm{m}^2}{\mathrm{s}^2}$$

This is the unit we will use the most. Actually, one joule is a fairly wimpy amount and chemical reactions tend to account for thousands of these. So we tack on "kilo-" and label it a kJ for one thousand J's.

Another energy unit which was used a lot in science years ago is the calorie (cal). Its use faded in chemistry with the adoption of the SI joule. It's a bit bigger than a joule: one calorie is defined to be exactly 4.184 J. On the kilo scale, one kcal is 4.184 kJ. Now, be careful here. This older science calorie is not the same as a nutritional Calorie (Cal). Although we sometimes capitalize nutritional "Calorie" to distinguish it from the older science "calorie" (lower case c), this is not always done. Here's the distinction between the two: one nutritional Calorie is equal to one thousand of the older science calories. That means one Cal = one kcal. This can get confusing, so be careful when working with these units. I have no idea of how that came about, but just think: that candy bar of 400 Calories is really 400,000 calories.

And remember: those Calories came from the Sun.

18.3 Terminology and such

The area of science which deals with energy gets real picky about terminology. We'll start into some of that right now.

The general area of energy is called thermodynamics. The "thermo-" prefix has the usual dictionary meaning and it refers to heat. (You know other words with the thermo- prefix, such as thermometer and thermostat.) The "-dynamics" part is also in a normal dictionary sense, referring to motion and/or forces behind motion. Thus, we can say that thermodynamics is the study of the motion or the flow of energy. And that goes for any form of energy, not just thermal energy. The term "thermochemistry" deals with chemistry aspects of thermodynamics and either of these terms is fine for our purposes.

The thing to keep in mind here is the sense of energy flow. Remember that this is Nature's cash flow. Energy flow is the transaction amount for some process. It's the payment paid or received.

There are two terms which have a somewhat specific meaning but which are derived from normal words: "system" and "surroundings". The system is the sample under study. It will undergo some change. It's whatever we define it to be for the study at hand. It can be some neutralization reaction in a beaker. It can be the combustion of hydrogen in air. It can even be something as simple as an ice cube melting. The surroundings are the environment of the sample. On a practical basis, the surroundings can be taken as the immediate environment with which the sample interacts or, technically, the surroundings can be the rest of the universe. Keep in mind the economic aspects. Transactions will occur between the system and its surroundings, by whatever way these are defined for the study at hand. Let's go back to money: you are the system, the store is the surroundings. Pick any kind of store you want. For me, it's hardware and tool stuff. If you're like many at a store, there will be a cash flow between the system (you) and the surroundings (store). Purchases represent cash flow out of the system (you) and into the surroundings (store). Returns represent cash flow into the system (you) and out of the surroundings (store). Notice that transactions can go either way, although stores drag more out of us than they give back.

The study of energy transactions can be conducted under a variety of conditions. This is important, since the conditions of the experiment can have an impact on the total amount of energy involved. The full characterization of any system makes up the "state" of the system. This includes the identities of the substances which are present, their phases, their amounts, and the conditions such as temperature and pressure. For a solute in solution, this will also include its concentration. Different states have different energies. Our emphasis will be in the energy transferred when some initial state (of some initial total amount of energy) undergoes some reaction or other process to form some final state (of some final total amount of energy). The difference in the energies between those two states will be the total transaction energy.

While the difference in the energies of the initial and final states determines the total transaction energy, it is possible in many cases to break that total down into various forms of energy. Historically, the breakdown was into a heat component and a work component. Much of thermodynamics dates back to the days of steam engines and the efforts at the time to understand the conversion of chemical (combustion) energy into heat (thermal) energy and work (mechanical) energy. This remains important even today, well typified by the automobile combustion engine: the chemical energy of the combustion process is again released as heat and work; while the engine gets hot and releases heat, the high pressure of the hot gas products from the combustion pushes a piston inside a cylinder, which then turns a crankshaft which eventually turns the wheels. Nowadays, the other forms of energy can also be involved, such as the conversion of chemical energy into electrical energy as occurs in batteries. Regardless of the various forms of energy which may be involved, the total transaction energy stays the same. This is what I meant upstairs.

> For any transaction, you begin with some amount of assets and you end with some amount of assets, and the difference is the transaction amount or cash flow... It does not matter if you dealt in paper bills, coins, checks or whatever. The only really important factors are what you start with, what you end with, and the transaction amount. These three are related arithmetically. We can write this as
>
> transaction amount = final assets – initial assets

We can now say:

> For any reaction or process, you begin with some amount of energy in the initial state and you end with some amount of energy in the final state, and the difference is the transaction amount or energy flow... It does not matter if you dealt in heat, mechanical, electrical or whatever. The only really important factors are what you start with, what you end with, and the transaction amount. These three are related arithmetically. We can write this as
>
> transaction amount = final state energy – initial state energy

The transaction amount is the sum of the various forms (heat, mechanical, electrical or whatever) of energy which are involved in a particular reaction or process. You can change the manner of conducting the reaction, and get a different distribution of the various forms (heat, mechanical, electrical or whatever) of energy, but the total transaction amount remains the same.

Overall, as we proceed here, the really important aspect is the transaction amount of the process. Overall, we want to know how many total joules pass between the system and the surroundings. For example, we want to know how many J's we get out of a neutralization reaction. Or, we want to know how many J's we get out of the combustion of hydrogen. Or, we want to know how many J's we must pay in order to melt an ice cube. And remember, flow can go either way: you either get J's out or you put J's in. But how much? That's the transaction amount. That's the energy flow. THAT'S WHAT WE WANT TO KNOW!

In chemistry, there are two common sets of conditions for measuring an energy flow. These have given rise to two terms for energy, called "internal energy" and "enthalpy". Both of these are a measure of the energy possessed by a system. What's really important is the transaction amount for a given reaction or process, and internal energy and enthalpy are meant for different conditions of that measurement. Measurements for internal energy involve a closed container of fixed volume; under those conditions, the pressure can change. Measurements for enthalpy are at a fixed pressure; under those conditions, the volume can change. The primary differences between the two arise when the reactants and products involve different amounts of gases; otherwise, the two methods give very similar results. I won't go further into those details although your instructor may. The bottom line for the here and now is that internal energy and enthalpy are a measure of the total energy possessed by a system in its initial state and the total energy possessed in the final state. Internal energy gets the symbol U; some people use E but E gets used for various other energy terms also. The use of U for the symbol appears to have been a somewhat arbitrary selection of a letter. Enthalpy gets the symbol H. The word is of Greek origin and is related to heat; the symbol H apparently derives from the word "heat" or another language's word for heat. Although enthalpy was originally connected to heat, it can include other forms of energy depending on the manner of conducting a reaction or process.

By the way, H's and U's are often called "state functions" because they are a function of the state of the system. For whatever set of conditions are specified for a particular state of a particular system, then the internal energy and the enthalpy are fixed for those conditions. If you change any of the conditions, then the amounts of internal energy and enthalpy can change (although changes in pressure have very small effects on solids, liquids and solutions).

That much ends my coverage for internal energy. We now proceed using enthalpy. Since many reactions and processes occur open to the atmosphere, then the system stays at a constant pressure (equal to the surrounding air pressure), which makes it convenient to deal with enthalpy.

A change or difference in anything is given the symbol of capital Greek delta, Δ. For thermodynamic things, the delta-change is always defined as the final amount minus the initial amount; this applies to any unit you're talking about. Keep this in mind: it's always final minus initial. Don't get it backwards or it'll screw things up.

$$\Delta(\text{whatever}) = \text{final whatever} - \text{initial whatever}$$

Remember the economic aspects

$$\text{transaction amount} = \text{final assets} - \text{initial assets}$$

which means we can write the following.

$$\Delta(\text{assets}) = \text{final assets} - \text{initial assets}$$

For enthalpy,

$$\Delta H = \text{final enthalpy} - \text{initial enthalpy}$$

which we can write as follows.

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

Δ's can be positive or negative, and this is very important. Let's say your assets are \$248. Let's say you purchase something for \$10, leaving your assets at \$238. The change is –\$10.

$$\Delta(\text{assets}) = \text{final} - \text{initial} = \$238 - \$248 = -\$10$$

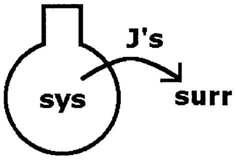
That negative sign is important. It tells you that your assets went down during the process. Now, let's go the other way. Your assets are \$248 and you make a return for \$15, leaving you with \$263.

$$\Delta(\text{assets}) = \text{final} - \text{initial} = \$263 - \$248 = \$15$$

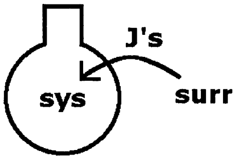
The change is \$15, positive. Your assets went up during the process. Thus, signs are important and you need to understand how these work.

- Every time you pay \$'s, your final assets are less than what you started with; the transaction amount for you is negative to reflect this.
- Every time you get \$'s, your final assets are more than you started with; the transaction amount for you is positive.

J's work the same way. If the system gives J's to the surroundings, then the transaction amount is negative and the system ends with less J's than it started with. This type of process is called exothermic. If the system obtains J's from the surroundings, then the transaction amount is positive and the system ends with more J's than it started with. This type of process is called endothermic. These are important terms, so get used to them. An easy way to distinguish them is that exo goes with exit and endo goes with into. For an exothermic process, J's exit the system and, for an endothermic process, J's go into the system. Let's summarize these relationships. The flasks represent the system (sys) of study; outside the flask are the surroundings (surr).



exothermic (J's exit system)
system gives J's to surroundings
enthalpy of the system decreases
$H_{\text{final}} < H_{\text{initial}}$
ΔH is negative



endothermic (J's into system)
system gets J's from surroundings
enthalpy of the system increases
$H_{\text{final}} > H_{\text{initial}}$
ΔH is positive

Remember that the sign of a Δ is very important. The sign gives the direction of the flow. Positive means the system gains, and the flow is into the system. Negative means the system loses, and the flow is out of the system.

Throughout all of these discussions, keep in mind the conservation of energy. The total J's between the system and the surroundings stay the same. J's don't just appear and disappear. If the system loses 5 J, then those 5 J are out there in the surroundings. Energy is conserved. And, like always, mass is conserved. Grams are conserved. Joules are conserved. Together, it's the conservation of mass-energy, or the conservation of g's and J's.

I had noted upstairs that H's are "state functions" because they are a function of the state of the system. It is also true that simple arithmetic derivations of state functions are also state functions. Thus, we can now add that ΔH's are state functions. Once the conditions of the process are defined, then the ΔH is a fixed amount; if you change any aspect of the final or initial states, then ΔH changes.

This wraps up the introductory terminology and background. It is really important that you understand this much so far. Next, we'll start working with chemical systems.

18.4 Thermochemical examples

We begin looking at the application of thermodynamics to chemical and physical processes and reactions. As we continue from here, notice that we define the process or reaction to be the system and that we will be outside, as part of the surroundings. If we want the reaction (the system) to provide J's to us (in the surroundings), then we want an exothermic reaction. On the other hand, if the reaction is endothermic, then we (or another part of the surroundings) must pay the J's into the reaction in order for it to do what we expect it to do.

Let's start in on some examples.

Combustions are very familiar for releasing energy in various forms such as heat, work and light (and even sound in an explosion). Let's talk about the combustion of H_2. Up to now, we have been concerned only with the mass aspect as given by the following equation.

$$2\ H_2(g)\ +\ O_2(g)\ \rightarrow\ 2\ H_2O(g)$$

Now we bring in the energy aspect. This reaction releases considerable energy, meaning energy is a product; we can incorporate this into the equation itself.

$$2\ H_2(g)\ +\ O_2(g)\ \rightarrow\ 2\ H_2O(g)\ +\ \text{energy}$$

That energy leaves the system and is passed to the surroundings. This is an exothermic reaction. For the reaction as written, the actual amount of energy for the transaction is 483.66 kJ.

$$2\ H_2(g)\ +\ O_2(g)\ \rightarrow\ 2\ H_2O(g)\ +\ 483.66\ \text{kJ}$$

This means that, for the combustion of two moles of hydrogen gas with one mole of oxygen gas to form two moles of water gas, the system releases 483.66 kJ to the surroundings. 483.66 kJ is a considerable amount, capable of seriously damaging a vehicle. Many chemical reactions are on the scale of hundreds of kJ's. Some are less, some are more.

Let me make a few comments here with just this very first example. This reaction is a simple combustion. Combustions are a primary source of energy used by human societies for centuries, and these have massive global impact, good and bad. Although hydrogen is not a universal fuel (yet), this example illustrates the exothermic nature of typical combustions and it illustrates our ability to quantify the energy associated with these processes using thermochemical principles. We can tap into that energy to do things if we wish. Of course, there is a price which human society pays for this. Commonly it is said that there is no free energy. That is true when "free" means no monetary cost. On the other hand, in chemistry there is a term called free energy but, in that sense, "free" means available. Free energy is the amount of energy which is theoretically available from a reaction or process. We talk about free energy in Chapter 45 and we'll see what else is involved. (It's entropy again.) For now, we only consider the energy associated with the enthalpy change of a reaction.

Now let's consider an endothermic case. We'll evaporate some water. This is a simple phase change, which we can also examine in terms of energy flow.

$$H_2O(l)\ \rightarrow\ H_2O(g)$$

You already know that it takes heat to boil water. Well, it also takes heat to evaporate water just at room temperature. Boiling and evaporation are both examples of vaporization. We can show the requirement for energy by including energy on the left of the equation.

$$\text{energy}\ +\ H_2O(l)\ \rightarrow\ H_2O(g)$$

This says that energy must go into the system and that it will be used up during the process, just like any other reactant. The heat must come from the surroundings in order for this process to occur. The amount involved is modest: 44.00 kJ for vaporization at 25 °C and one atm (or, technically, one bar).

$$44.00\ \text{kJ}\ +\ H_2O(l)\ \rightarrow\ H_2O(g)$$

In other words, if you start with one mole (18.02 g) of liquid water at 25 °C and evaporate the whole thing to water vapor at 25 °C, the surroundings must pay 44.00 kJ. The surroundings lose energy, typically involving heat, which typically causes some cooling in the surroundings.

Nature designed your body to utilize this endothermic phase change. After all, that's why you sweat: it cools you down. Here's what happens. Think of the sweat as the system and your skin as part of the surroundings. Sweat is mostly water. The water on the skin evaporates to gas phase. The evaporation process costs J's and your skin pays those J's. The water molecules take those J's with them as they leave into the air around you. Your skin loses those J's as heat, and your skin cools down. That's Nature's cooling system for humans. It can be slow, unless a good wind is blowing. If you want a more dramatic demonstration, use rubbing alcohol. As we've discussed in prior Chapters, this is 70% isopropyl alcohol. Rubbing alcohol evaporates much faster than water alone, so the loss of J's from your skin occurs much faster and you feel cooler quicker. Just don't use too much because the stuff is flammable. We're talking about evaporation right now, not combustion.

There's another ramification to point out about this phase change business. Phases are an important part of the characterization of the state of the system. The phases themselves differ in the total energy assets which are inherent to them. In other words, one mole of $H_2O(l)$ has a different amount of total energy than one mole of $H_2O(g)$, even when they're both at the same temperature. It's got to do with the makeup of the phases themselves. The difference in the energies between the phases is equal to the transaction amount for the phase change. From above, we know that we have to add 44.00 kJ to one mole of $H_2O(l)$ in order to get one mole of $H_2O(g)$. So, one mole of gas-phase H_2O at 25 °C possesses 44.00 kJ more in its energy assets than one mole of liquid-phase H_2O at 25 °C. This is a general property of all compounds: gas phases always pack more energy than liquid phases, even when they are at the same temperature.

By the way, because the energy amounts differ for different phases, we now have to get specific about phases every time we deal with the energetics of a reaction. Although I've been loose about showing phases in chemical equations ever since Chapter 6, now we need them.

As we continue along, remember: a J is a J is a J. Whether chemical, heat, mechanical or electrical, it's all energy and the forms are interconvertible. If heat J's go into a system, then the system can get hotter, but if those same J's are converted to chemical J's or to mechanical J's or to electrical J's, then the temperature need not change. The J's are still in there, as required by the conservation of energy, but they're in a different form. This is one part that bothers a lot of students since they only think of energy as heat. J's ARE NOT JUST HEAT. Highlight that sentence. It's important to remember.

Let's do some more explanation with the combustion of H_2 from above.

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$$

I'll also specify temperature and pressure for this. The system begins with 2 mol $H_2(g)$ and 1 mol $O_2(g)$, with each at 25 °C and one atm. (The volumes are fixed by *PVnRT*.) After everything is all done and over, the system is composed of 2 mol $H_2O(g)$ at 25 °C and one atm. Now, let's take a look at the energies for the initial and final states.

2 mol $H_2(g)$
25 °C, one atm

1 mol $O_2(g)$
25 °C, one atm

INITIAL

The initial package has some total assets of energy as a result of having two moles of H_2 and one mole of O_2, along with the energies of those molecules, and due to the fact that those molecules are gas phase (as opposed to some other phase), and due to the fact that they are all at 25 °C and one atm. Add up all such factors and you get the total enthalpy of the starting package, which we designate H_{initial}.

2 mol $H_2O(g)$
25 °C, one atm

FINAL

This final package has some total assets of energy due to the fact that two moles of H_2O are present along with the energies of those molecules, and due to the fact that those molecules are gas phase (as opposed to another phase), and due to the fact that they are at 25 °C and one atm. Add up all such factors and you get the total enthalpy of this package, which we designate H_{final}.

Notice that I threw in the bit about the energies of the molecules themselves. This energy primarily arises from the fact that different molecules have different bonds with different energies. During a reaction, some bonds are broken and new ones are made. That's a big part of the total energy of a chemical reaction, although other factors can also contribute. We'll see more about these bond energies in Chapter 25 and in Chapter 27.

The difference between the final package and the initial package is the transaction amount for the process, or the energy flow, as defined for the system.

$$\Delta H_{\text{sys}} = H_{\text{final}} - H_{\text{initial}}$$

We can also call it the change in the enthalpy of the reaction, which is designated simply as ΔH.

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

As mentioned above for this reaction, 483.66 kJ are involved in the transaction. These J's are lost from the system and they go to the surroundings. The system ends with less J's than it started with, which can be expressed as $H_{\text{final}} < H_{\text{initial}}$. The reaction is exothermic and ΔH is negative.

$$\Delta H = H_{\text{final}} - H_{\text{initial}} = -483.66 \text{ kJ}$$

Having gone through this whole spiel, now I must tell you something ironic: we don't know what the values are for H_{final} and H_{initial}! We can't measure them! But we can measure ΔH, and that's really what we need to know anyway. I'll repeat what I said earlier.

> And remember, flow can go either way: you either get J's out or you put J's in. But how much? That's the transaction amount. That's the energy flow. THAT'S WHAT WE WANT TO KNOW.

It's ΔH that counts. It's not the separate H's. It's the difference that matters.

I want to come back to the temperature and pressure business because there are often questions about that. We're talking about combustion. I said we start at 25 °C and we end at 25 °C; we start at one atm for each gas and we end at one atm. Many students wonder how in the world do you combust something at a steady temperature and pressure? Well, there was a catch in the way I worded it.

The change in the system is determined by how the system starts (initial state) and how the system ends (final state). The difference in energy is ΔH. It does not matter how you execute the reaction. It does not matter how many steps you do it in. The overall, net difference is the same. And that's the only thing that matters.

Let's see how this applies to our combustion. Start with 2 mol $H_2(g)$ and 1 mol $O_2(g)$ at 25 °C and one atm, each in their own container. That's the initial state for the system. Combine them and then blow them up. Let's say it gets real hot and hits 500 °C inside the container after detonation, releasing some J's to the surroundings in the process. Now, let it continue to release J's to the surroundings until it comes back to 25 °C. Pressure can also vary during the process as long as it, too, is returned to one atm at the end. That's the final state for the system. Add up all those J's, including the J's released from initial detonation and the J's released while returning to 25 °C, along with any J's associated with returning pressure to one atm: you'll get the same total, 483.66 kJ. Now let's imagine that we do the reaction slowly and keep the system at 25 °C and one atm all along the way. (Yes, this is possible.) Add up the total J's which are released to the surroundings over the whole process: you'll get the same amount of 483.66 kJ. The only thing that matters is where the system starts and where the system ends; the difference between those two is the overall, net change. That's ΔH.

How can different ways result in the same total transaction energy? Here's the catch: different ways of executing a reaction can result in different, relative amounts of the various forms of energy (heat, mechanical, electrical or whatever) which are involved. For example, exploding the mixture releases a lot of energy as heat energy, but running this same reaction in a fuel cell releases a lot of energy as electrical energy. (Fuel cell??? More in Chapter 64.) Regardless of the manner of operation, the total of the different forms of energy stays the same, and that's ΔH.

Although I said you get 483.66 kJ out of the reaction, remember that direction corresponds to the ± sign when a Δ is written. Thus, we write this as $\Delta H = -483.66$ kJ. Now we have two ways of showing energy for a balanced equation. The first way we did earlier

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) + 483.66 \text{ kJ}$$

and the second way is to write ΔH separately from the equation.

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \qquad \Delta H = -483.66 \text{ kJ}$$

Here's a bit of warning about wording for exothermic cases. When you read or hear terms such as "483.66 kJ's are released" or "483.66 kJ's are given off" or similar such wording, then these terms tell you direction: kJ's exit the system. The amount "released" or "given off" is a number without a negative sign. On the other hand, when you specifically say ΔH equals some number, then you must show the negative sign. Compare the following statements for the above reaction.

- The reaction releases 483.66 kJ.
- The reaction gives off 483.66 kJ.
- For the reaction, $\Delta H = -483.66$ kJ.

All of these statements say the same thing. All mean an exothermic process.

OK, so much for exothermic. For a different illustration, let me refer back to our endothermic example from above: the vaporization of water. We can write it as we did upstairs

$$44.00\ \text{kJ} + H_2O(l) \rightarrow H_2O(g)$$

or we can write ΔH separately.

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H = 44.00\ \text{kJ}$$

I had presented this to you earlier as starting at 25 °C and ending at 25 °C. In order for this to happen, the surroundings must pay 44.00 kJ into the system (the water). Again, those J's pay for evaporation; in the end, they do not change the water's temperature. Even though the J's might come from heat energy, that heat energy did not change the temperature because the J's were converted into the chemical energy of the gas phase for that H_2O.

Here's a very important point which you need to understand: heat need not mean hot. Yes, adding heat energy to an object can make it hotter, but adding heat energy to pay for an endothermic process does not necessarily make the system hotter. And it is also possible for a colder object to have more heat than a hotter object. These notions can be a bit tricky. I'll elaborate upon these things in the next section. This next section is a bit of a side-step but I'm doing it to make a point and to bring in some related aspects.

18.5 Can you take the heat?

Before heat, let me talk about hot.

The words "hot" and "cold" are used in normal conversation in the same way as "young" and "old" are used. They're relative terms, they are not absolute terms. They're relative to a point of reference which depends on what you're talking about. Most people on Earth might think I'm old, but there are yet some who might think I'm young. Who's right? It depends on your frame of reference. I was born in 1954, and that leads to my actual or absolute age in years. Age is an absolute term with a specific definition. Young and old are simply relative terms.

Hot and cold are also relative terms. On the other hand, heat is an actual amount of thermal energy. Let's say you have a cup of water at 60 °C and a bathtub full of water at 25 °C. Which one is hot? Which one has more heat? We would say that the cup of water was hot, but the bathtub of water has more heat. Don't believe it? Go see for yourself: here's a simple experiment, based on common experience. You know that it takes heat to melt an ice cube. How many ice cubes will the cup of water melt? How many ice cubes will the bathtub of water melt? The one that melts more ice cubes had more heat. It's that simple.

We gauge hot and cold by temperature, but you must remember that cold things do have heat. The temperature of a sample is actually a function of three parameters: the thermal energy possessed by the sample, the size of the sample, and the identity of the sample. For a specific object, the sample size and its identity are fixed and constant, but its thermal energy can change; that's what changes the temperature of the object. For a given object, this relationship is termed heat capacity and that relationship is a proportionality.

$$\text{change in thermal energy} \propto \text{change in } T$$

We can write this as

$$\text{change in thermal energy} \propto \Delta T$$

where

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

So far, this relationship for change in thermal energy is only for a specific object; let's generalize this relationship for any object of any identity and of any size. For this, I want to introduce at this time a special symbol, q, for the thermal J's put into or released by a system. Be careful with this symbol: q is defined as the amount of J's transferred only as heat.

For a sample of a pure compound, its size can be expressed either as a mass amount or as a number of moles of substance. Both ways are common; some instructors cover one or the other and some cover both. I will use mass (g) for sample size. The starting point for developing our general relationship is then the following.

$$q \propto \Delta T \times \text{mass}$$

In order to turn this into an equality, we need to introduce a proportionality constant. This proportionality constant will be some value which depends on the identity of the substance.

$$q = \Delta T \times \text{mass} \times \text{proportionality constant (based on identity)}$$

The proportionality constant is symbolized *c* and it is called the specific heat capacity. Its value is specific to a specific compound.

$$q = \Delta T \times \text{mass} \times c$$

We can re-arrange this to

$$c = \frac{q}{\text{mass} \bullet \Delta T}$$

This represents the number of J's required to change the temperature of one gram of the substance by one degree. For example, the specific heat capacity for $H_2O(l)$ is 4.18 J/(g • K), which means that it will cost you 4.18 J to raise the temperature of one gram of water by one K. We can compare that to some other liquid, such as CCl_4, which has a specific heat capacity of 0.85 J/(g • K): it will cost 0.85 J to raise the temperature of one gram of carbon tetrachloride by one K. Every different compound has a different specific heat capacity because every different compound responds to heat energy differently.

Here's another re-arrangement of the above equations.

$$\Delta T = \frac{q}{\text{mass} \bullet c}$$

This version allows you to calculate how much a sample's temperature will change for some transfer of heat energy into or out of the sample.

Let me make a small point here about temperature scales. Changing temperature by one K is the same as changing temperature by one °C, since the size of the kelvin and the size of the Celsius degree were set up the same. For this reason, these values can also be written as 4.18 J/(g • °C) for water and 0.85 J/(g • °C) for CCl_4. When you do the ΔT part, you can do it either as K or °C. For example, if a sample's temperature increases by 10 K, then it increases by 10 °C.

Technically, the values of specific heat capacity depend on temperature by themselves. The values above are for *c* at 298 K (25 °C). The temperature dependence is small, so using a certain number for *c* for different temperatures within a modest temperature range is common practice. Sometimes an average is used. It's not really a big deal for what we need, but just be aware that different problems at different temperatures could use slightly different values for *c*.

In all of these, the term *q* is defined for the system. We will again have ± signs for direction and these ± signs will also show up in ΔT. The specific heat capacity and the mass are always positive.

$$\begin{array}{lccccccc} & q & = & \Delta T & \times & \text{mass} & \times & c \\ & \uparrow & & \uparrow & & & & \\ \text{Sample gains heat:} & (+) & & (+) & & & & \\ \text{Sample loses heat:} & (-) & & (-) & & & & \end{array}$$

To illustrate, let's go back to the water example. Putting 4.18 J <u>into</u> ($q = +4.18$ J) one gram of water makes it hotter by 1 K (or by 1 °C). Conversely, you can take 4.18 J <u>out of</u> ($q = -4.18$ J) one gram of water, and it would get colder by 1 K (°C). Everything is proportional: if it's two grams or if it changes temperature by two K, then it's two × 4.18 J = 8.36 J.

This leads into calculations of how many J's are involved for heating and cooling any item from one temperature to another. To illustrate this process, let's return to our cup of hot water and the bathtub of water as mentioned above. In this way, you'll really get to see who has more heat. We'll set up this comparison with each as a separate system.

- We define System A as one cup (237 mL) of water at 60. °C. At this temperature, water has a density of 0.988 g/mL, so the sample mass is 234 g.
- We define System B as a bathtub of water at 25 °C. We'll assume a volume of 30.0 gallons (113 L). At this temperature, the density of water is 0.997 g/mL, so the sample mass is 113,000 g.

Now we dump ice into each separate system. For our purposes here, we define the starting water as the system and the ice as the surroundings. The water in Systems A and B will transfer J's to their ice, causing some to melt, until everything reaches 0. °C. Once everything is at 0. °C, then there will be no more net transfer of J's and melting will be done. When done, System A and System B will be at T_{final} = 0. °C, and you end up with a cup of ice water and a bathtub of ice water. (In the real world, you would also take into account J's from the cup itself and from the tub itself. To keep things easier, I defined everything only for the water and the ice, so that's all we need for the illustration here.) We have two calculations to do and they're just plug-and-chug. Let's set them up. We'll use 4.2 J/(g • °C) for *c* for water in these temperature ranges.

$$q = \Delta T \times \text{mass} \times c$$

- System A, Cup of Water mass = 234 g

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 0.\ ^\circ\text{C} - 60.\ ^\circ\text{C} = -60.\ ^\circ\text{C}$$

Plug it in.

$$q = -60.\ ^\circ\text{C} \times 234\ \text{g} \times 4.2\,\frac{\text{J}}{\text{g} \bullet {}^\circ\text{C}} = -59{,}000\ \text{J} = -59\ \text{kJ}$$

This says that the water in System A transfers 59 kJ to the ice.

- System B, Bathtub of Water mass = 113,000 g

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 0.\ ^\circ\text{C} - 25\ ^\circ\text{C} = -25\ ^\circ\text{C}$$

Plug it in.

$$q = -25\ ^\circ\text{C} \times 113{,}000\ \text{g} \times 4.2\,\frac{\text{J}}{\text{g} \bullet {}^\circ\text{C}} = -12{,}000{,}000\ \text{J} = -12{,}000\ \text{kJ}$$

This says that the water in System B transfers 12,000 kJ to the ice.

Here's the grand conclusion. Although System A starts hotter, it only has 59 kJ available to deliver to the ice before everything ends at 0. °C. On the other hand, System B has far more heat available (12,000 kJ) due to its far greater size. Thus, System B will melt much more ice. That brings me to the point which I was making: heat does not necessarily mean hot. In this example, the colder sample had more heat than the hotter sample.

Let me wrap up a few things. Remember this part.

Earlier in this Chapter, we talked about reactions involving heat transfer, but the system began and ended at the same temperature. Here in this section, we talked about J's transferring into or out of a system to make it hotter or colder. Overall, these are THE ONLY TWO POSSIBLE OUTCOMES WHEN TRANSFERRING J'S INTO OR OUT OF A SYSTEM.

- A transfer of J's can result in or result from an endothermic or exothermic process. Under these conditions, the temperature need not change.
- If no endothermic or exothermic process occurs, then a transfer of J's must result in a change in temperature.

Here's another way of looking at this. You cannot put J's into a system and have nothing happen at all. Either the J's must pay for an endothermic process to occur or the system's temperature must go up. (A combination of the two is possible.) The J's are an investment in the system: the J's are contained within the chemical make-up of the molecules and phases or they are contained within the temperature and the available heat of the system. By reversing the process or by letting the system cool, the J's can be fully recovered from the system.

That's all part of the conservation of energy.

Problems

1. True or false.
   a. One calorie is more energy than one joule.
   b. For an exothermic process, the system ends with more energy than it had originally.

c. The combustion of gasoline is endothermic.

d. One mol of $H_2O(l)$ has more energy than one mol of $H_2O(g)$ (at the same temperature and pressure).

e. An endothermic process can absorb heat energy without changing temperature.

2. True or false.

a. The energy of a system depends on the state of the system.

b. During an endothermic process, joules are transferred from the surroundings into the system.

c. If the system's ΔH is positive, then the system loses energy.

d. The melting of ice is exothermic.

e. When an object cools, it loses heat energy.

3. Ice cubes are placed in a small container with 940. g of warm (35 °C) water. Some ice melts until the contents of ice + water reach 0. °C. (Ignore any heat involving the container.) What is the value for q (in kJ) for the original warm water? The specific heat capacity for water in this temperature range is 4.2 J/(g • K).

4. A 4.9 g sample of ethyl alcohol, C_2H_5OH, originally at 19 °C, absorbs 140 J of heat. What is the change in temperature (in °C) for this process? What is the final temperature (in °C) of the ethyl alcohol? The specific heat capacity for C_2H_5OH in this temperature range is 2.4 J/(g • K).