Chemical Energetics

All about enthalpy, calorimetry and the First Law of Thermodynamics

A Chem1 Reference Text

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This document covers the basics of chemical thermodynamics, the First Law, and thermochemistry at a level appropriate for first-year college chemistry. It was last modified on 23 December 2003 .

All chemical changes are accompanied by the absorption or release of heat. The intimate connection between matter and energy has been a source of wonder and speculation from the most primitive times; it is no accident that fire was considered one of the four basic elements (along with earth, air, and water) as early as the fifth century BCE. In this unit we will review some of the fundamental concepts of energy and heat and the relation between them. We will begin the study of ***thermodynamics***[1], which treats the energetic aspects of change in general, and we will finally apply this specifically to chemical change. Our purpose will be to provide you with the tools to predict the energy changes associated with chemical processes. This will build the groundwork for a more ambitious goal: to predict the direction and extent of change itself.

One of the interesting things about thermodynamics is that although it deals with matter, it makes no assumptions about the microscopic nature of that matter. Thermodynamics deals with matter in a macroscopic sense; it would be valid even if the atomic theory of matter were wrong. This is an important quality, because it means that reasoning based on thermodynamics is unlikely to require alteration as new facts about atomic structure and atomic interactions come to light.

1 Energy

Energy is one of the most fundamental and universal concepts of physical science, but one that is remarkably difficult to define in way that is meaningful to most people. This perhaps reflects the fact that energy is not a “thing” that exists by itself, but is rather an attribute of matter (and also of electromagnetic radiation) that can manifest itself in different ways. It can be observed and measured only indirectly through its effects on matter that acquires, loses, or possesses it.

Kinetic energy and potential energy

Whatever energy may be, there are basically two kinds: kinetic and potential[2]. ***Kinetic energy*** **is associated with the motion of an object**; a body with a mass m and moving at a velocity v possesses the kinetic energy

$$mv^2/2.$$

Potential energy ***is energy a body has by virtue of its location in a force field.*** The most common kinds of force fields are gravitational, electrical, or magnetic. For example, if an object of mass m is raised off the floor to a height h, its potential energy increased by mgh, where g is a proportionality constant known as the *acceleration of gravity.*

You might at first think that a book sitting on the table has zero kinetic energy since it is not moving. In truth, however, that the earth itself is moving; it is spinning on its axis, it is orbiting the sun, and the sun itself is moving away from the other stars in the general expansion of the universe. Since these motions are normally of no interest to us, we are free to adopt an arbitrary scale in which the velocity of the book is measured with respect to the table; on this so-called *laboratory coordinate system*, the kinetic energy of the book can be considered zero.

We do the same thing with potential energy. If the book is on the table, its potential energy with respect to the surface of the table will be zero. If we adopt this as our zero of potential energy, and then push the book off the table, its potential energy will be negative after it reaches the floor.

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[1] This term comes from the Greek words referring to the movement of heat.

[2] In the 17th century, the great mathematician Leibniz suggested the distinction between *vis viva* (“live energy” and *vis mortua* “dead energy”, which gradually became kinetic and potential energy.

Energy scales and units

Energy is measured in terms of its ability to perform work or to transfer heat. ***Mechanical work*** is done when a force *f* displaces an object by a distance *d*: $w = f \times d$. The basic unit of energy is the *joule*. One joule is the amount of work done when a force of 1 newton acts over a distance of 1 m; thus 1 J = 1 N-m. The newton is the amount of force required to accelerate a 1-kg mass by 1 m/sec^2, so the basic dimensions of the joule are kg m^2 s^{-2}.The other two units in wide use, the calorie and the BTU (British thermal unit), are defined in terms of the heating effect on water. Because of the many forms that energy can take, there are a correspondingly large number of units in which it can be expressed. A few of these are summarized in Table 1.

1 **calorie** will raise the temperature of 1 g of water by 1 C°. The "dietary" calorie is actually 1 kcal.	1 cal = 4.184 J 1 J = 0.24 cal
1 **BTU** (British Thermal Unit) will raise the temperature of 1 lb of water by 1F°.	1 BTU = 1055 J
The **er**g is the c.g.s. unit of energy and a very tiny one; the work done when a 1-dyne force acts over a distance of 1 cm.	1 J = 1 × 10^7 erg 1 erg = 1 d-cm = 1 g cm^2 s^{-2}
1 **electron-volt** is the work required to move a unit electric charge (1 C) through a potential difference of 1 volt.	1 J = 6.24 × 10^{18} eV
The *watt* is a unit of *power*, which measures the *rate* of energy flow in J sec^{-1}. Thus the **watt-hour** is a unit of energy. An average human consumes energy at a rate of about 100 watts; the brain alone runs at about 5 watts.	1 J = 2.78 × 10^{-4} watt-hr 1 w-h = 3.6 kJ
The liter-atmosphere is a variant of force-displacement work associated with volume changes in gases.	1 L-atm = 101.325 J
The huge quantities of energy consumed by cities and countries are expressed in **quads**; the **therm** is a similar but smaller unit.	1 quad = 10^{15} Btu = 1.05 × 10^{18} J 1 therm = 10^5 Btu
If the object is to obliterate cities or countries with nuclear weapons, the energy unit of choice is the **ton of TNT equivalent**.	1 ton of TNT = 4.184 GJ (by definition)
In terms of **fossil fuels**, we have **barrel-of-oil** equivalent, cubic-meter-of-natural gas equivalent, and ton-of-coal equivalent.	1 bboe = 6.1 GJ 1 cmge = 37-39 MJ 1 toce = 29 GJ

Table 1: Some commonly-encountered energy units

2 Basic thermodynamics: what you need to know

2.1 Systems and surroundings

The thermodynamic view of the world requires that we be very precise about our use of certain words. The two most important of these are *system* and *surroundings.* A ***thermodynamic system*** is that part of the world to which we are directing our attention. Everything that is not a part of the system constitutes the ***surroundings***. The system and surroundings are separated by a ***boundary***. If our system is one mole of a gas in a container, then the boundary is simply the inner wall of the container itself. The boundary need not be a physical barrier; for example, if our system is a factory or a forest, then the boundary can be wherever we wish to define it. We can even focus our attention on the dissolved ions in an aqueous solution of a salt, leaving the water molecules as part of the surroundings. The single property that the boundary must have is that it be clearly defined, so we can unambiguously say whether a given part of the world is in our system or in the surroundings.

If matter is not able to pass across the boundary, then the system is said to be ***closed***; otherwise, it is ***open***. A closed system may still exchange energy with the surroundings unless the system is an ***isolated*** one, in which case neither matter nor energy can pass across the boundary. The tea in a closed Thermos bottle approximates a closed system over a short time interval.

2.2 Properties and the state of a system

The ***properties*** of a system are those quantities such as the pressure, volume, temperature, and its composition, which are in principle measurable and capable of assuming definite values. There are of course many properties other than those mentioned above; the density and thermal conductivity are two examples. However, the pressure, volume, and temperature have special significance because they determine the values of all the other properties; they are therefore known as ***state properties*** because if their values are known then the system is in a definite ***state***.

Change of state: the meaning of delta In dealing with thermodynamics, we must be able to unambiguously define the change in the state of a system when it undergoes some process. This is done by specifying changes in the values of the different state properties as illustrated here for a change in the volume:

$$\Delta V = V_{final} - V_{initial}$$

We can compute similar delta-values for changes in P, V, n_i (the number of moles of component *i*), and the other state properties we will meet later.

2.3 Heat and work

Heat and work are both measured in energy units, so they must both represent energy. How do they differ from each other, and from just plain “energy” itself?

First, recall that energy can take many forms: mechanical, chemical, electrical, radiation (light), and thermal, or heat. So ***heat*** is a form of energy, but it differs from all the others in one crucial way. All other forms of energy are interconvertible: mechanical energy can be completely converted to electrical energy, and the latter can be completely converted to heat. However, ***complete conversion of heat into other forms of energy is impossible.*** This is the essence of the *Second Law of Thermodynamics* which is covered in another unit; for the moment, we will simply state that this fact places heat in a category of its own and justifies its special treatment.

There is another special property of heat that you already know about: heat can be transferred from one body (i.e., one *system*) to another. We often refer to this as a *flow of heat,* recalling the 18th-century notion that heat was an actual substance called "*caloric*" that could flow like a liquid. Moreover, you know that heat can only flow from a system at a higher temperature to one at a lower temperature. This special characteristic is often used to distinguish heat from other modes of transferring energy across the boundaries of a system.

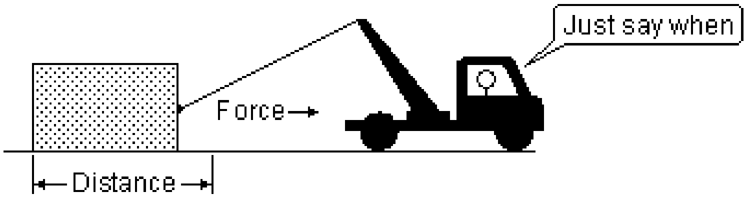
Work, like energy, can take various forms: mechanical, electrical, gravitational, etc. All have in common the fact that they are the product of two factors, an intensity term and a capacity term. For example, the simplest form of *mechanical work* arises when an object moves a certain *distance* against an opposing *force*. *Electrical work* is done when a body having a certain *charge* moves through a *potential difference*.

type of work	*intensity term*	*capacity term*	*formula*
mechanical	force	change in distance	$f \Delta x$
gravitational	gravitational potential	mass	$mg\ h$
electrical	potential difference	quantity of charge	$Q\ \Delta E$

Table 2: Capacity and intensity factors in various kinds of work

Mechanical work is the product of the force exerted on a body and the distance it is moved: 1 N-m = 1 J

(Illustration from www.benwiens.com/energy1.html)

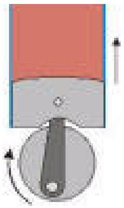


Performance of work involves a transformation of energy; thus when a book drops to the floor, gravitational work is done (a mass moves through a gravitational potential difference), and the potential energy the book had before it was dropped is converted into kinetic energy which is ultimately dispersed as heat.

Heat and work are best thought of as *processes* by which energy is exchanged, rather than as energy itself. That is, heat "exists" only when it is flowing, work "exists" only when it is being done.

*When two bodies are placed in thermal contact and energy flows from the warmer body to the cooler one, we call the process "**heat**". A transfer of energy to or from a system by any means other than heat is called "**work**".*

Interconvertability of heat and work



Work can be completely converted into heat (by friction, for example), but heat can only be partially converted to work. This is accomplished by means of a *heat engine*. The science of thermodynamics developed out of the need to understand the limitations of steam-driven heat engines at the beginning of the Industrial Age. A fundamental law of Nature, the *Second Law of Thermodynamics*, states that the complete conversion of heat into work is impossible. Something to think about when you purchase fuel for your car!

2.4 Internal energy

Internal energy is simply the totality of all forms of kinetic and potential energy of the system. Thermodynamics makes no distinction between these two forms of energy and it does not assume the existence of atoms and molecules. But since we are studying thermodynamics in the context of chemistry, we can allow ourselves to depart from "pure" thermodynamics enough to point out that the internal energy is the sum of the kinetic energy of motion of the molecules, and the potential energy represented by the chemical bonds between the atoms and any other intermolecular forces that may be operative.

How can we know how much internal energy a system possesses? The answer is that we cannot, at least not on an absolute basis; all scales of energy are arbitrary. The best we can do is measure *changes* in energy. However, we are perfectly free to define zero energy as the energy of the system in some arbitrary reference state, and then say that the internal energy of the system in any other state is the difference between the energies of the system in these two different states.

2.5 The First Law of thermodynamics.

This law is one of the most fundamental principles of the physical world. Also known as the ***Law of Conservation of Energy***, it states that energy can not be created or destroyed; it can only be redistributed or changed from one form to another[1]. A way of expressing this law that is generally more useful in Chemistry is the sum

$$\Delta U = q + w \qquad (1)$$

This says that there are two kinds of processes, heat and work, that can lead to a change in the internal energy of a system. Since both heat and work can be measured and quantified, this is the same as saying that any change in the energy of a system must result in a corresponding change in the energy of the world outside the system- in other words, *energy cannot be created or destroyed*.

> There is an important *sign convention* for heat and work that you are expected to know. If heat flows into a system or the surroundings to do work on it, the internal energy increases and the sign of q or w is positive. Conversely, heat flow out of the system or work done by the system will be at the expense of the internal energy, and will therefore be negative. (Note that this is the opposite of the sign convention that was commonly used in the pre-1970 literature.)

The full significance of Eq. 1 cannot be grasped without understanding that U is a ***state function***. This means that a given change in internal energy ΔU can follow an infinite variety of pathways reflected by all the possible combinations of q and w that can add up to a given value of ΔU.

> As a simple example of how this principle can simplify our understanding of change, consider two identical containers of water initially at the same temperature. We place a flame under one until its temperature has risen by 1°C. The water in the other container is stirred vigorously until its temperature has increased by the same amount. There is now no physical test by which you could determine which sample of water was warmed by performing work on it, by allowing heat to flow into it, or by some combination of the two processes. In other words, there is no basis for saying that one sample of water now contains more "work", and the other more "heat". The only thing we can know for certain is that both samples have undergone identical increases in internal energy, and we can determine the value of simply by measuring the increase in the temperature of the water.

2.6 Pressure-volume work

The kind of work most frequently associated with chemical change occurs when the volume of the system changes owing to the disappearance or formation of gaseous substances. This is sometimes called *expansion work* or *PV*-work, and it can most easily be understood by reference to the simplest form of matter we can deal with, the ideal gas.

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[1] An early statement of energy conservation by René Descartes (1596-1650) explained that in creating the world, God established "vortices", states of motion that could interact and be transformed, but which in their totality would endure in perpetuity.

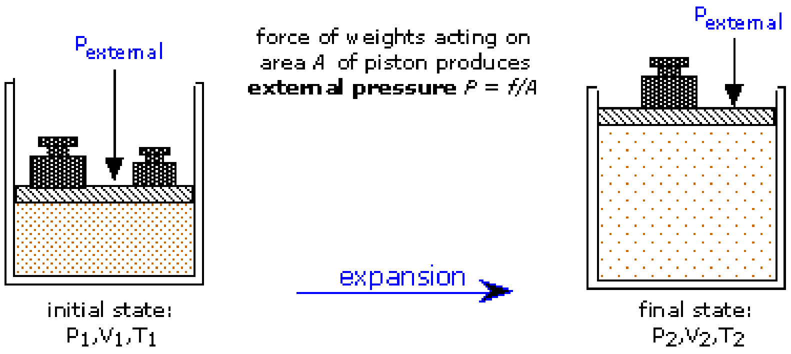

Fig. 1: Expansion of a gas subjected to a constant external pressure

The figure shows a quantity of gas confined in a cylinder by means of a moveable piston. Weights placed on top of the piston exert a force *f* over the cross-section area *A*, producing a pressure $P = f / A$ which is exactly countered by the pressure of the gas, so that the piston remains stationary. Now suppose that we heat the gas slightly; according to Charles' law, this will cause the gas to expand, so the piston will be forced upward by a distance Δx. Since this motion is opposed by the force *A*, a quantity of work $f\Delta x$ will be done by the gas on the piston. By convention, work done by the system (in this case, the gas) on the surroundings is negative, so the work is given by

$$w = -f\Delta x$$

When dealing with a gas, it is convenient to think in terms of the more relevant quantities pressure and volume rather than force and distance. We can accomplish this by multiplying the second term by *A/A* which of course leaves it unchanged:

$$w = (-f)(\Delta x) \times \frac{A}{A}$$

By grouping the terms differently, but still not changing anything, we obtain

$$w = \left(\frac{f}{A}\right)(\Delta x) \times A$$

Since pressure is force per unit area and the product of the length A and the area has the dimensions of volume, this expression becomes

$$w = -P\,\Delta V \qquad (2)$$

This equation is a good illustration of how a non-state function like the work depends on the path by which a given change is carried out. In this case the path is governed by the *external pressure P.*

Problem Example 1

Find the amount of work done on the surroundings when 1 liter of an ideal gas, initially at a pressure of 10 atm, is allowed to expand at constant temperature to 10 liters by *a)* reducing the external pressure to 1 atm in a single step, *b)* reducing *P* first to 5 atm, and then to 1 atm, *c)* allowing the gas to expand into an evacuated space so its total volume is 10 liters.

Solution. First, note that ΔV, which is a state function, is the same for each path:
$V_2 = (10/1) \times (1\text{ L}) = 10\text{ L}$, so $\Delta V = 9$ L.

For path *(a)*, $w = -(1\text{ atm}) \times (9\text{ L}) = -9$ L-atm.

For path *(b)*, the work is calculated for each stage separately:

$w = -(5\text{ atm}) \times (2-1\text{ L}) - (1\text{ atm}) \times (10-2\text{ L}) = -13$ L-atm

For path *(c)* the process would be carried out by removing all weights from the piston in Fig. 1 so that the gas expands to 10 L against zero external pressure. In this case $w = (0\text{ atm}) \times 9\text{ L} = 0$; that is, no work is done because there is no force to oppose the expansion.

2.7 Adiabatic and isothermal processes

When a gas expands, it does work on the surroundings; compression of a gas to a smaller volume similarly requires that the surroundings to do work on the gas. If the gas is thermally isolated from the surroundings, then the process is said to occur *adiabatically*. In an adiabatic change, $q = 0$, so the First Law becomes $\Delta U = 0 + w$. Since the temperature of the gas changes with its internal energy, it follows that adiabatic compression of a gas will cause it to warm up, while adiabatic expansion will result in cooling.

In contrast to this, consider a gas in a container immersed in a constant-temperature bath. As the gas expands, it does work on the surroundings and therefore tends to cool, but this causes heat to pass into the gas from the surroundings to exactly compensate for this change. This is called an isothermal expansion. In an isothermal process the internal energy remains constant and we can write the First Law as $0 = q + w$, or $q = -w$, illustrating that the heat flow and work done exactly balance each other.

Because no thermal insulation is perfect, truly adiabatic processes do not occur. However, heat flow does take time, so a compression or expansion that occurs more rapidly than thermal equilibration can be considred adiabatic for practical purposes.

If you have ever used a hand pump to inflate a bicycle tire, you may have noticed that the bottom of the pump barrel can get quite warm. Although a small part of this warming may be due to friction, it is mostly a result of the work you (the surroundings) are doing on the system (the gas.)

Adiabatic expansion and contractions are especially important in understanding the behavior of the atmosphere. Although we commonly think of the atmosphere as homogeneous, it is really not, due largely to uneven heating and cooling over localized areas. Because mixing and heat transfer between adjoining parcels of air does not occur rapidly, many common atmospheric phenomena can be considered at least quasi-adiabatic. A more detailed exposition of this topic is given in Section 5 of this unit.

2.8 Reversible processes

The preceding example shows clearly how the work, a non-state function, depends on the manner in which a process is carried out.

From Problem Example 1 we see that when a gas expands into a vacuum ($P_{external} = 0$). the work done is zero. This is the minimum work the gas can do; what is the *maximum work* the gas can perform on the surroundings? To answer this, notice that more work was done when the process was carried out in two stages than in one stage, and a simple calculation will show that even more work can be obtained by increasing the number of stages— that is, by allowing the gas to expand against a series of successively lower external pressures. In order to extract the maximum possible work from the process, the expansion would have to be carried out in an infinite sequence of infinitessimal steps. Each step yields an increment of work $P\,\Delta V$ which can be expressed as $(RT/V)\,dV$ and integrated:

$$w = -\int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln \frac{V_1}{V_2}$$

Although such a path (which corresponds to what is called a ***reversible process)*** cannot be realized in practice, it can be approximated as closely as desired.

Even though no real process can take place reversibly (it would take an infinitely long time!), reversible processes play an essential role in thermodynamics. The main reason for this is that q_{rev} and w_{rev} are state functions which are important and are easily calculated. Moreover, many real processes take place sufficiently gradually that they can be treated as approximately reversible processes for easier calculation.

These plots illustrate the effects of various degrees of reversibility on the amount of work done when a gas expands, and the work that must be done in order to restore it to its initial state by recompressing it. The work, in each case, is proportional to the shaded area on the plot.

Each expansion-compression cycle leaves the gas unchanged, but in all but the one in the bottom row, the surroundings are forever altered, having expended more work in compressing the gas than was performed on it when the gas expanted.

Only when the processes are carried out in an infinite number of steps will the system and the surroundings be restored to their initial states— this is the meaning of thermodynamic reversibility.

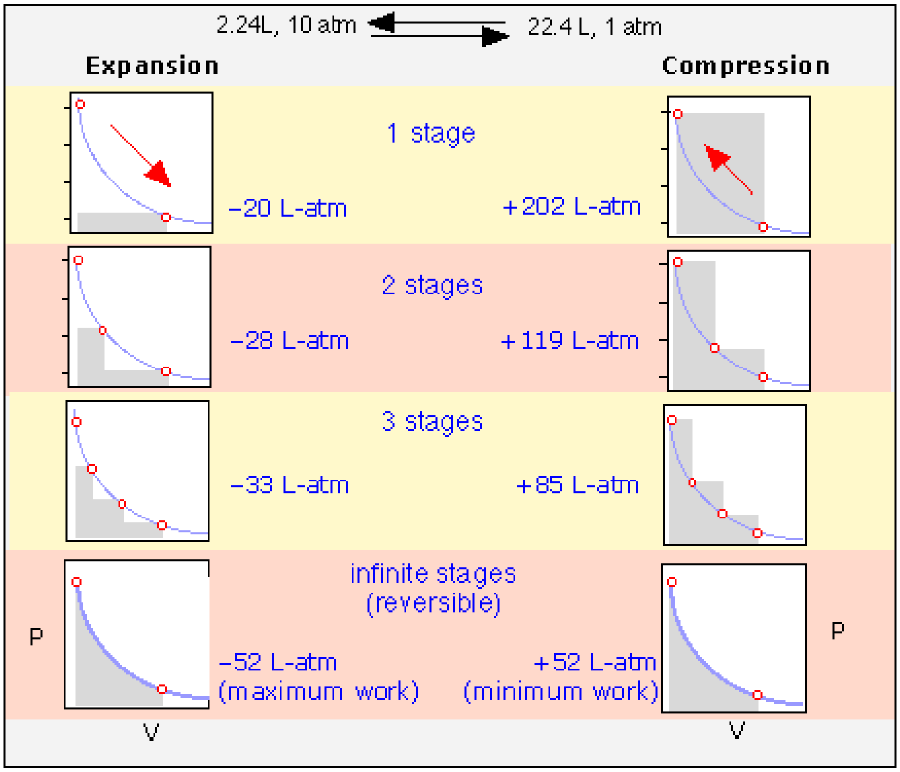

Fig. 2: Work associated with multi-stage expansions and compressions

3 Heat changes at constant pressure: the enthalpy

Most chemical processes are accompanied by changes in the volume of the system, and therefore involve both heat and work terms. If the process takes place at a constant pressure, then the work is given by $P\Delta V$ and the change in internal energy will be

$$\Delta U = q - P\Delta V \qquad (3)$$

Thus the amount of heat that passes between the system and the surroundings is given by

$$q = \Delta U + P\Delta V \qquad (4)$$

Problem Example 2

Hydrogen chloride gas readily dissolves in water, releasing 75.3 kJ/mol of heat in the process. If one mole of HCl at 298 K and 1 atm pressure occupies 24.5 liters, find the ΔU for the system when one mole of HCl dissolves in water under these conditions.

Solution: In this process the volume of liquid remains practically unchanged, so $\Delta V = -24.5$ L. The work done is

$$w = -P\Delta V = -(1\text{ atm})(-24.5\text{ L}) = 24.6\text{ L-atm}$$

(The work is positive because it is being done *on* the system as its volume decreases due to the dissolution of the gas into the much smaller volume of the solution.) Using the conversion factor 1 L-atm = 101.33 J mol^{-1} and substituting in Eq. 3 (Page 11) we obtain

$$\Delta U = q + P\Delta V = -(75300\text{ J}) + [101.33\text{ J/L-atm}) \times (24.5\text{ L-atm})] = -72.82\text{ kJ}$$

In other words, if the gaseous HCl simply dissolved without volume change, the heat released by the process (75.3 kJ) would cause the system's internal energy to diminish by 75.3 kJ. But the volume decrease due to the disappearance of the gas is equivalent to compression of the system by the pressure of the atmosphere; the resulting work done on the system acts to increase its internal energy, so the net value of ΔU is –72.82 kJ instead of –75.3 kJ.

Since both ΔU and ΔV in Eq 4 are state functions, then q_P, the heat that is absorbed or released when a process takes place at constant pressure, must also be a state function and is known as the ***enthalpy change*** **ΔH**.

$$\Delta H \equiv q_P = \Delta U + P\Delta V \qquad (5)$$

Since most changes that occur in the laboratory, on the surface of the earth, and in organisms are subjected to a constant pressure of one atmosphere, Eq 5 is the form of the First Law that is of greatest interest to most scientists.

3.1 The heat capacity

For systems in which no change in composition (chemical reaction) occurs, things are even simpler: to a very good approximation, the enthalpy depends only on the temperature. This means that ***the temperature of such a system can serve as a direct measure of its enthalpy***. The functional relation between the internal energy and the temperature is given by the ***heat capacity*** measured at constant pressure:

$$C_P = \frac{dH}{dT} \qquad (6)$$

(or $\Delta H/\Delta T$ if you don't care for calculus!) An analogous quantity relates the heat capacity at constant volume to the internal energy:

$$C_V = \frac{dU}{dT}$$

The difference between C_P and C_V is of importance only when the volume of the system changes significantly— that is, when different numbers of moles of gases appear on either side of the chemical equation. For reactions involving only liquids and solids, Cp and Cv are for all practical purposes identical.

Heat capacity can be expressed in joules or calories per mole per degree (molar heat capacity), or in joules or calories per gram per degree; the latter is called the *specific* heat capacity or just the ***specific heat***.

The greater the heat capacity of a substance, the smaller will be the effect of a given absorption or loss of heat on its temperature.

substance	c J/g-K	C J/mol-K
aluminum	.900	24.3
copper	.386	24.5
lead	.128	26.5
mercury	.140	28.3
zinc	.387	25.2
alcohol (ethanol)2.4	2.4	111
water	4.186	75.2
ice (–10° C)	2.95	36.8
gasoline (*n*-octane)	.53	2.22
glass	.84	
carbon (graphite / diamond)	.157 / .147	7.88 / 7.38
rock (granite)	.79	
air	1.006	

Table 3: Heat capacities of some substances

Note especially:

- The molar heat capacities of the **metallic elements** are almost identical. This is the basis of the *Law of Dulong and Petit*, which served as an important tool for extimating the atomic weights of these elements.
- The **intermolecular hydrogen bonding** in water and alcohols results in anomalously high heat capacities for these liquids; the same is true for ice, compared to other solids.
- The values for graphite and diamond are consistent with the principle that solids that are more "ordered" tend to have larger heat capacities.

4 Molecules as energy carriers and converters

All molecules at temperatures above absolue zero possess *thermal energy*— the randomized kinetic energy associated with the various motions the molecules as a whole, and also the atoms within them, can undergo. Polyatomic molecules also possess *potential energy* in the form of chemical bonds. Molecules are thus both vehicles for storing energy and moving it around, and the means of converting it from one form to another when the formation, breaking, or rearrangement of the chemical bonds within them is accompanied by the uptake or release of heat.

4.1 Chemical Energy

When you buy a liter of gasoline for your car, a cubic meter of natural gas to heat your home, or a small battery for your flashlight, you are purchasing energy in a chemical form. In each case, some kind of a chemical change will have to occur before this energy can be released and utilized: the fuel must be burned in the presence of oxygen, or the two poles of the battery must be connected through an external circuit (thereby initiating a chemical reaction inside the battery.) And eventually, when each of these reactions is complete, our source of energy will be exhausted; the fuel will be used up, or the battery will be “dead”.

Chemical substances are made of atoms, or more generally, of positively charged nuclei surrounded by negatively charged electrons. A molecule such as dihydrogen, H_2, is held together by electrostatic attractions mediated by the electrons shared between the two nuclei. The total potential energy of the molecule is the sum of the repulsions between like charges and the attractions between electrons and nuclei:

$$PE_{total} = PE_{electron\text{-}electron} + PE_{nucleus\text{-}nucleus} + PE_{nucleus\text{-}electron}$$

In other words, ***the potential energy of a molecule depends on the time-averaged relative locations of its constituent electrons and nuclei .*** This dependence is expressed by the familiar potential energy curve which serves as an important description of the chemical bond between two atoms.

In gaseous hydrogen, for example, H_2 the molecules will be moving freely from one location to another; this is called translational motion, and the molecules therefore possess translational kinetic energy $KE_{trans} = m\bar{v}^2/2$, in which $\bar{v}$ stands for the average velocity of the molecules; you may recall from your study of gases that $\bar{v}$, and therefore KE_{trans}, depends on the temperature.

In addition to translation, molecules can possess other kinds of motion. Because a chemical bond acts as a kind of spring, the two atoms in H_2 will have a *natural vibrational frequency.* In more complicated molecules, many different modes of vibration become possible, and these all contribute a *vibrational* term KE_{vib} to the total kinetic energy. Finally, a molecule can undergo *rotational* motions which give rise to a third term KE_{rot}. Thus the total kinetic energy of a molecule is the sum

$$KE_{total} = KE_{trans} + KE_{vib} + KE_{rot}$$

The total energy of the molecule is just the sum

$$E_{total} = KE_{total} + PE_{total} \tag{7}$$

Although this formula is simple and straightforward, it cannot take us very far in understanding and predicting the behavior of even one molecule, let alone a large number of them. The reason, of course, is the chaotic and unpredictable nature of molecular motion. Fortunately, the behavior of a large collection of molecules, like that of a large population of people, can be described by statistical methods.

4.2 How molecules take up thermal energy

As noted above, the *heat capacity* of a substance is a measure of how sensitively its temperature is affected by a change in heat content; the greater the heat capacity, the less effect a given flow of heat q will have on the temperature. We also pointed out that temperature is a measure of the average kinetic energy due to translational motions of molecules. If vibrational or rotational motions are also active, these will also accept thermal energy and reduce the amount that goes into translational motions. Because the temperature depends only on the latter, the effect of the other kinds of motions will be to reduce the dependence of the internal energy on the temperature, thus raising the heat capacity of a substance.

Vibrational and rotational motions are not possible for monatomic species such as the noble gas elements, so these substances have the lowest heat capacities. Moreover, as you can see in the leftmost column of Table 4, their heat capacities are all the same. This reflects the fact that translational motions are the same for all particles; all such motions can be resolved into three directions in space, each contributing one *degree of freedom* to the molecule and 1/2 R to its heat capacity. (R is the gas constant, 8.314 J K^{-1}).

Polyatomic molecules

monatomic		diatomic		triatomic	
He	20.5	CO	29.3	H_2O	33.5
Ne	20.5	N_2	29.3	D_2O	34.3
Ar	20.5	F_2	31.4	CO_2	37.2
Kr	20.5	Cl_2	33.9	CS_2	45.6

Table 4: Molar heat capacities of some gaseous substances at constant pressure

Whereas monatomic molecules can only possess translational thermal energy, two additional kinds of motions become possible in polyatomic molecules. A *linear* molecule has an axis that defines two perpendicular directions in which rotations can occur; each represents an additional degree of freedom, so the two together contribute a total of 1/2 R to the heat capacity. For a non-linear molecule, rotations are possible along all three directions of space, so these molecules have a rotational heat capacity of 3/2 R. Finally, the individual atoms within a molecule can move relative to each other, producing a v*ibrational* motion. A molecule consisting of N atoms can vibrate in $3N$–6 different ways or *modes*[1]. For mechanical reasons that we cannot go into here, each vibrational mode contributes R (rather than 1/2 R) to the total heat capacity.

		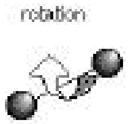	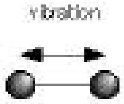
monatomic	3/2 R	0	0
diatomic	3/2 R	R	1
polyatomic	3/2 R	3/2 R	$3N$–6
separation between adjacent levels, per mol	6.0×10^{-17} J (O_2)	373 J (HCl)	35 kJ (HCl)

Table 5: Contribution of molecular motions to heat capacity

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[1] This result comes from advanced mechanics and will not be proven here.

Now we are in a position to understand why more complicated molecules have higher heat capacities. The total kinetic energy of a molecule is the sum of those due to the various kinds of motions:

$$KE_{total} = KE_{trans} + KE_{rot} + KE_{vib}$$

When a monatomic gas absorbs heat, all of the energy ends up in translational motion, and thus goes to increase its temperature. In a polyatomic gas, by contrast, the absorbed energy is partitioned among the other kinds of motions; since only the translational motions contribute to the temperature, the temperature rise is smaller, and thus the heat capacity is larger.

There is one very significant complication, however: classical mechanics predicts that the energy is always partitioned equally between all degrees of freedom. Experiments, however, show that this is observed only at quite high temperatures. The reason is that these motions are all *quantized*. This means that only certain increments of energy are possible for each mode of motion, and unless a certain minimum amount of energy is available, a given mode will not be active at all and will contribute nothing to the heat capacity.

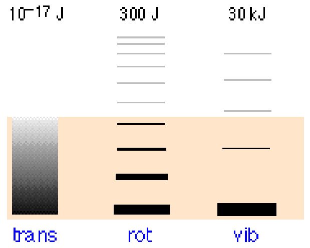

Fig. 3a: Distribution of thermal energy in a typical diatomic molecule

The relative occupancy of the rotational and vibrational states is indicated by the thickness of the lines. At 300K, virtually all molecules are in their lowest vibrational state and in the first 2 or 3 rotational states; nearly all the thermal energy is contained in the translational states which essentially form a continuum.

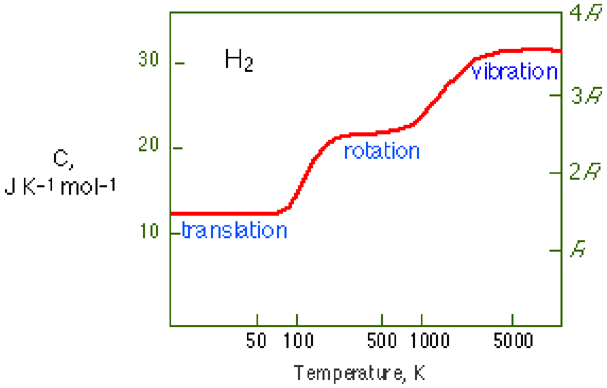

Fig. 2b: Heat capacity as a function of temperature for dihydrogen

It turns out that translational energy levels are spaced so closely that they these motions are active almost down to absolute zero, so all gases possess a heat capacity of at least 3/2 *R* at all temperatures. Rotational motions do not get started until intermediate temperatures, typically 300-500K, so within this range heat capacities begin to increase with temperature. Finally, at very high temperatures, vibrations begin to make a significant contribution to the heat capacity.

The strong intermolecular forces of liquids and many solids allow heat to be channeled into vibrational motions involving more than a single molecule, further increasing heat capacities. One of the well known “anomalous” properties of liquid water is its high heat capacity (75 J mol^{-1} K^{-1}) due to intermolecular hydrogen bonding, which is directly responsible for the moderating influence of large bodies of water on coastal climates (see page 30.)

Heat capacities of metals Metallic solids are a rather special case. In metals, the atoms oscillate about their equilibrium positions in a rather uniform way which is essentially the same for all metals, so they should all have about the same heat capacity. That this is indeed the case is embodied in the ***Law of Dulong and Petit***. In the 19th century these workers discovered that the molar heat capacities of all the metallic elements they studied were around to 25 J mol^{-1} K^{-1}, which is close to what classical physics predicts for crystalline metals. This observation played an important role in characterizing new elements, for it provided a means of estimating their molar masses by a simple heat capacity measurement.

5 Energetics of chemical reactions

The rearrangement of atoms that occurs in a chemical reaction is virtually always accompanied by the liberation or absorption of heat. If the purpose of the reaction is to serve as a source of heat, such as in the combustion of a fuel, then these heat effects are of direct and obvious interest. We will soon see, however, that a study of the energetics of chemical reactions in general can lead us to a deeper understanding of chemical equilibrium and the basis of chemical change itself.

In chemical thermodynamics, we define the zero of the enthalpy and internal energy as that of the elements as they exist in their stable forms at 298K and 1 atm pressure. Thus the enthalpies H of Xe*(g)*, O_2*(g)* and C*(diamond)* are all zero, as are those of H_2 and Cl_2 in the reaction

$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$$

The enthalpy of two moles of HCl is smaller than that of the reactants, so the difference is released as heat. Such a reaction is said to be ***exothermic***. The reverse of this reaction would absorb heat from the surroundings and be ***endothermic***.

In comparing the internal energies and enthalpies of different substances as we have been doing here, it is important to compare equal numbers of moles, because energy is an extensive property of matter. However, heats of reactions are commonly expressed on a molar basis and treated as *intensive* properties.

5.1 Changes in enthalpy and internal energy

We can characterize any chemical reaction by the change in the internal energy or enthalpy:

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

The significance of this can hardly be exaggerated because ΔH, being a ***state function***, is entirely independent of *how* the system gets from the initial state to the final state. In other words, the value of ΔH or ΔU for a given change in state is independent of the ***pathway*** of the process.

Consider, for example, the oxidation of a lump of sugar to carbon dioxide and water:

$$C_{12}H_{22}O_{11} + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(l)$$

This process can be carried out in many ways, for example by burning the sugar in air, or by eating the sugar and letting your body carry out the oxidation. Although the mechanisms of the transformation are entirely different for these two pathways, the overall change in the enthalpy of the system (the atoms of carbon, hydrogen and oxygen that were originally in the sugar) will be identical, and can be calculated simply by looking up the enthalpies of the reactants and products (see page 19) and calculating the difference

$$\Delta H = 12 \times H(CO_2) + 11 \times H(H_2O) - H(C_{12}H_{22}O_{11}) = -5606 \text{ kJ}$$

The same quantity of heat is released whether the sugar is burnt in the air or oxidized in a series of enzyme-catalyzed steps in your body.

5.2 Variation of the enthalpy with temperature

The enthalpy of a system increases with the temperature by the amount $\Delta H = C_P \Delta T$. The defining relation

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

tells us that this change is dominated by the internal energy, subject to a slight correction for the work associated with volume change. Heating a substance causes it to expand, making ΔV positive and causing the enthalpy to increase slightly more than the internal energy. Physically, what this means is that if the temperature is increased while holding the pressure constant, some extra energy must be expended to push back the external atmosphere while the system expands. The difference between the dependence of U and H on temperature is only really significant for gases, since the coefficients of thermal expansion of liquids and solids are very small.

Phase changes

A plot of the enthalpy of a system as a function of its temperature is called an *enthalpy diagram.* The slope of the line is given by C_p. The enthalpy diagram of a pure substance such as water shows that this plot is not uniform, but is interrupted by sharp breaks at which the value of C_p is apparently infinite, meaning that the substance can absorb or lose heat without undergoing any change in temperature at all. This, of course, is exactly what happens when a substance undergoes a phase change; you already know that the temperature the water boiling in a kettle can never exceed 100 until all the liquid has evaporated, at which point the temperature of the steam will rise as more heat flows into the system.

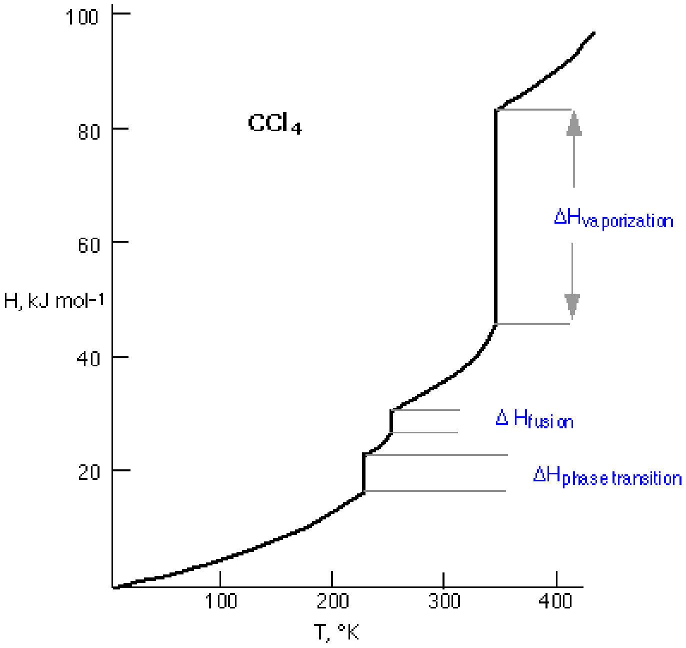

Fig. 4: Enthalpy of carbon tetrachloride as a function of temperature at 1 atm

A plot of the enthalpy of a system as a function of its temperature provides a concise view of its thermal behavior. The slope of the line is given by C_p. The enthalpy diagram of a pure substance such as water shows that this plot is not uniform, but is interrupted by sharp breaks at which the value of C_p is apparently infinite, meaning that the substance can absorb or lose heat without undergoing any change in temperature at all. This, of course, is exactly what happens when a substance undergoes a *phase change;* you already know that the temperature of the water boiling in a kettle can never exceed 100°C until all the liquid has evaporated, at which point the temperature (of the steam) resumes its increase as more heat flows into the system.

The lowest-temperature discontinuity on the CCl_4 diagram corresponds to a *solid-solid phase transition* associated with a rearrangement of molecules in the crystalline solid.

Fusion and boiling are not the only kinds of phase changes that matter can undergo. Most solids can exist in different structural modifications at different temperatures, and the resulting solid-solid phase changes produce similar discontinuities in the heat capacity. Enthalpy diagrams are easily determined by following the temperature of a sample as heat flows into our out of the substance at a constant rate. The resulting diagrams are widely used in materials science and forensic investigations to characterize complex and unknown substances.

6 Thermochemistry

The heat that flows across the boundaries of a system undergoing a change is a fundamental property that characterizes the process. It is easily measured, and if the process is a chemical reaction carried out at constant pressure, it can also be predicted from the difference between the enthalpies of the products and reactants. The quantitative study and measurement of heat and enthalpy changes is known as ***thermochemistry***.

6.1 Thermochemical equations and standard states

In order to define the thermochemical properties of a process, it is first necessary to write a *thermochemical equation* that defines the actual change taking place, both in terms of the formulas of the substances involved and their physical states (temperature, pressure, and whether solid, liquid, or gaseous.

To take a very simple example, here is the complete thermochemical equation for the vaporization of water at its normal boiling point:

$$H_2O(l, 373\text{ K}, 1\text{ atm}) \rightarrow H_2O(g, 373\text{ K}, 1\text{ atm}) \qquad \Delta H = 40.7\text{ kJ mol}^{-1}$$

The quantity 40.7 is known as the ***enthalpy of vaporization*** ("heat of vaporization") of liquid water.

The following points should be kept in mind when writing thermochemical equations:

- Thermochemical equations for reactions taking place in solution must also specify the concentrations of the dissolved species. For example, the enthalpy of neutralization of a strong acid by a strong base is

  $$H^+(aq, 1\underline{M}, 298\text{ K}, 1\text{ atm}) + OH^-(aq, 1\underline{M}, 298\text{ K}, 1\text{ atm}) \rightarrow H_2O(l, 373\text{ K}, 1\text{ atm}) \qquad \Delta H = 56.9\text{ kJ mol}^{-1}$$

  in which the abbreviation *aq* refers to the hydrated ions as they exist in aqueous solution. Since most thermochemical equations are written for the standard conditions of 298 K and 1 atm pressure, we can leave these quantities out if these conditions apply both before and after the reaction. If, under these same conditions, the substance is in its preferred (most stable) physical state, then the substance is said to be in its ***standard state***. Thus the standard state of water at 1 atm is the solid below 0°C, and the gas above 100°C. A thermochemical quantity such as ΔH that refers to reactants and products in their standard states is denoted by $\Delta H°$.
- In the case of **dissolved substances**, the standard state of a solute is that in which the "effective concentration", known as the ***activity,*** is unity. For non-ionic solutes the activity and molarity are usually about the same for concentrations up to about $1\underline{M}$, but for an ionic solute this approximation is generally valid only for solutions more dilute than $0.001\text{-}0.01\underline{M}$, depending on electric charge and size of the particular ion.
- Any thermodynamic quantity such as ΔH that is associated with a thermochemical equation always refers to the number of moles of substances explicitly shown in the equation. Thus for the synthesis of water we can write

  $$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l) \qquad \Delta H = -572\text{ kJ}$$

  or

  $$H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -286\text{ kJ}$$

6.2 Enthalpy of formation

The enthalpy change for a chemical reaction is the difference

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

If the reaction in question represents the formation of one mole of the compound from its elements in their standard states, as in

$$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -286 \text{ kJ}$$

then we can arbitrarily set the enthalpy of the elements to zero and write

$$H_f{}^\circ = \Sigma H_f{}^\circ{}_{\text{products}} - \Sigma H_f{}^\circ{}_{\text{reactants}} = -286 \text{ kJ} - 0 = -268 \text{ kJ mol}^{-1}$$

which defines the ***standard enthalpy of formation*** of water at 298K.

The standard enthalpy of formation of a compound is defined as the heat associated with the formation of one mole of the compound from its elements in their standard states.

In general, the standard enthalpy change for any reaction is given by the expression

$$\Delta H^\circ = \Sigma H_f{}^\circ{}_{\text{products}} - \Sigma H_f{}^\circ{}_{\text{reactants}}$$

in which the $\Sigma H_f{}^\circ$ terms indicate the sums of the standard enthalpies of formations of all products and reactants. **The above definition is one of the most important in chemistry because it allows us to predict the enthalpy change of any reaction without knowing any more than the standard enthalpies of formation of the products and reactants, which are widely available in tables.**

The following examples illustrate some important aspects of the standard enthalpy of formation of substances.

- The thermochemical equation defining $H_f{}^\circ$ is always written in terms of one mole of the substance in question:

  $$1/2\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g) \qquad \Delta H^\circ = -46.1 \text{ kJ mol}^{-1}$$

- A number of elements, of which sulfur and carbon are common examples, can exist in more then one solid crystalline form. The standard heat of formation of a compound is always taken in reference to the forms of the elements that are most stable at 25°C and 1 atm pressure. In the case of carbon, this is the *graphite*, rather than the *diamond* form:

  $$C(graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ = -393.5 \text{ kJ mol}^{-1}$$

  $$C(diamond) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ = -395.8 \text{ kJ mol}^{-1}$$

- The physical state of the *product* of the formation reaction must be indicated explicitly if it is not the most stable one at 25°C and 1 atm pressure:

  $$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H^\circ = -285.8 \text{ kJ mol}^{-1}$$

  $$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(g) \qquad \Delta H^\circ = -241.8 \text{ kJ mol}^{-1}$$

  Notice that the difference between these two ΔH° values is just the *heat of vaporization* of water.

- Although the formation of most molecules from their elements is an exothermic process, the formation of some compounds is mildly endothermic:

  $$1/2\ N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H^\circ = +33.2 \text{ kJ mol}^{-1}$$

  A positive heat of formation is frequently associated with instability— the tendency of a molecule to decompose into its elements, although it is not in itself a sufficient cause. In many cases, however, the rate of this decomposition is essentially zero, so it is still possible for the substance to exist. In this connection, it is worth noting that all molecules will become unstable at higher temperatures.

- The thermochemical reactions that define the heats of formation of most compounds cannot actually take place; for example, the direct synthesis of methane from its elements

$$C(graphite) + 2\ H_2(g) \rightarrow CH_4(g)$$

cannot be observed directly owing to the large number of other possible reactions between these two elements. However, the standard enthalpy change for such a reaction be found indirectly from other data, as explained in the next section.

- The standard enthalpy of formation of **gaseous atoms** from the element is known as the ***heat of atomization***. Heats of atomization are always positive, and are important in the calculation of bond energies.

  $Fe(s) \rightarrow Fe(g)$ $\Delta H° = 417$ kJ mol^{-1}

- The standard heat of formation of a **dissolved ion** such as Cl^- (that is, formation of the ion from the element) cannot be measured because it is impossible to have a solution containing a single kind of ion. For this reason, ***ionic enthalpies*** are expressed on a separate scale on which $H_f°$ of the hydrogen ion at unit activity (1 *M* effective concentration) is defined as zero. Thus for $Ca^{2+}(aq)$, $H_f° = –248$ kJ mol^{-1}; this means that the reaction

  $$Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-(aq)$$

  would release 248 kJ mol^{-1} more heat than the reaction

  $$1/2\ H_2(g) \rightarrow H^+(aq) + e^-(aq)$$

(Of course, neither of these reactions can take place by themselves, so ionic enthalpies must be measured indirectly.)

The standard enthalpy of formation the hydrogen ion is defined as zero

6.3 Hess' law and thermochemical calculations

You probably know that two or more chemical equations can be combined algebraically to give a new equation. Even before the science of thermodynamics developed in the late nineteenth century, it was observed by Germaine Hess (1802-1850) that the heats associated with chemical reactions can be combined in the same way to yield the heat of another reaction. For example, the standard enthalpy changes for the oxidation of graphite and diamond can be combined to obtain $\Delta H°$ for the transformation between these two forms of solid carbon, a reaction that cannot be studied experimentally.

$$C(graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H° = –393.51\text{ kJ mol}^{-1}$$

$$C(diamond) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H° = –395.40\text{ kJ mol}^{-1}$$

Subtraction of the second reaction from the first (i.e., writing the second equation in reverse and adding it to the first one) yields

$$C(graphite) \rightarrow C(diamond) \qquad \Delta H° = 1.89\text{ kJ mol}^{-1}$$

This principle, known as ***Hess' law of independent heat summation*** is a direct consequence of the enthalpy being a state function. Hess' law is one of the most powerful tools of chemistry, for it allows the change in the enthalpy (and in other thermodynamic functions) of huge numbers of chemical reactions to be predicted from a relatively small base of experimental data.

Because most substances cannot be prepared directly from their elements, heats of formation of compounds are seldom determined by direct measurement. Instead, Hess' law is employed to calculate enthalpies of formation from more accessible data. The most important of these are the standard *enthalpies of combustion*. Most elements and compounds combine with oxygen, and many of these oxidations are highly exothermic, making the measurement of their heats relatively easy.

For example, by combining the heats of combustion of carbon, hydrogen, and methane, we obtain the standard enthalpy of formation of methane, which as we noted above, cannot be determined directly:

$C(\textit{graphite}) + O_2(g) \rightarrow CO_2(g) \quad \Delta H° = –393.51\ \mathrm{kJ}$

$2\ H_2(g) + O_2(g) \rightarrow CH_4(g) \quad \Delta H° = –571.5\ \mathrm{kJ}$

$CO_2(g) + 2\ H_2O(l) \rightarrow CH_4(g) + O_2(g) \Delta H° = +784.3\ \mathrm{kJ}$

$\mathbf{C}(\textit{\textbf{graphite}}) \mathbf{+ 2\ H_2O}(g) \rightarrow \mathbf{CH_4}(g) \quad \Delta \boldsymbol{H}° = –74.4\ \kappa\vartheta$

The standard *heat of atomization* refers to the transformation of an element into gaseous atoms:

$C(graphite) \rightarrow C(g) \quad \Delta H° = 716.7\ \mathrm{kJ}$

... which is always, of course, an endothermic process. Heats of atomization are most commonly used for calculating bond energies.

6.4 Calorimetry

How are enthalpy changes determined experimentally? First, you must understand that the only thermal quantity that can be observed directly is the heat q that flows into or out of a reaction vessel, and that q is numerically equal to $\Delta H°$ only under the special condition of constant pressure. Moreover, q is equal to the standard enthalpy change only when the reactants and products are both at the same temperature, normally 25°C.

The measurement of q is generally known as ***calorimetry***. A very simple calorimetric determination of the standard enthalpy of the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

could be carried out by combining equal volumes of 0.1 solutions of HCl and of NaOH initially at 25°C. Since this reaction is exothermic, a quantity of heat q will be released into the solution, What we actually measure is the resulting temperature rise; if we multiply ΔT by the specific heat capacity of the solution, which will be close to that of pure water (4.184 J/g-K), we obtain the number of joules of heat released into each gram of the solution, and q can then be calculated from the mass of the solution. Since the entire process is carried out at constant pressure, we have $\Delta H° = q$.

For reactions that cannot be carried out in dilute aqueous solution, the reaction vessel is commonly placed within a larger insulated container of water. During the reaction, heat passes between the inner and outer containers until their temperatures become identical. Again, the temperature change of the water is observed, but in this case the value of q cannot be found just from the mass and the specific heat capacity of the water, for we now have to allow for the absorption of some of the heat by the walls of the inner vessel. Instead, the calorimeter is “calibrated” by measuring the temperature change that results from the introduction of a known quantity of heat. The resulting *calorimeter constant*, expressed in JK^{-1}, can be regarded as the “heat capacity of the calorimeter”. The known source of heat is usually produced by passing an electric current through a resistor within the calorimeter.

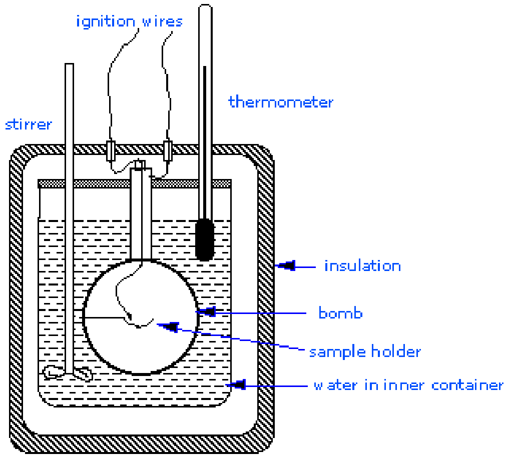

Fig. 5: Bomb calorimeter for measurement of heat of combustion.

Probably the most frequent kind of calorimetric measurement, especially of organic compounds, is the determination of *heats of combustion.* Such measurements present special problems owing to the gaseous nature of O_2 and CO_2, and the necessity of igniting the mixture in order to start the reaction. Since the gases must be confined, heat of combustion determinations are carried out under conditions of constant volume, rather of constant pressure, so what is actually measured in the internal energy change ΔU. The stoichiometry of the combustion reaction is used to calculate the change Δn_g in the number of moles of gas, and this is used to find $\Delta H°$:

$$\Delta H = \Delta U + \Delta(PV) = q_V + \Delta n_g RT \qquad (8)$$

Since the process takes place at constant volume, the reaction vessel must be constructed to withstand the high pressure resulting from the combustion process, which amounts to a confined explosion. The vessel is usually called a “bomb”, and the technique is known as ***bomb calorimetry***. In order to ensure complete combustion, the bomb is initially charged with pure oxygen above atmospheric pressure. The reaction is initiated by discharging a capacitor through a thin wire which ignites the mixture. The product of the capacitance and the voltage gives the quantity of charge, and thus the energy introduced into the calorimeter by the spark; this value is subtracted from that calculated from the observed temperature rise of the calorimeter to yield the heat of the combustion reaction. A more common practice is to determine the temperature rise produced by combustion, under identical conditions, of a substance whose heat of combustion is accurately known.

Problem Example 3

A sample of biphenyl $(C_6H_5)_2$ weighing 0.526 g was ignited in a bomb calorimeter initially at 25°C, producing a temperature rise of 1.91 K. In a separate calibration experiment, a sample of benzoic acid C_6H_5COOH weighing 0.825 g was ignited under identical conditions and produced a temperature rise of 1.94 K. For benzoic acid, the heat of combustion a constant pressure is known to be 3226 kJ mol^{-1} (that is, $\Delta U° = -3226$ kJ mol^{-1}.) Use this information to determine the standard enthalpy of combustion of biphenyl.

Solution. The calorimeter constant is given by

$$\frac{(-3226 \text{ kJ mol}^{-1})(.825 \text{ g})}{(1.94 \text{ K})(123 \text{ g mol}^{-1})} = -11.1 \text{ kJ K}^{-1}$$

The heat released by the combustion of the biphenyl is then

$$\frac{(-11.1 \text{ kJ K}^{-1})(1.94 \text{ K})\ (154 \text{ g mol}^{-1})}{.526 \text{ g}} = -6240 \text{ kJ mol}^{-1}$$

(The negative sign indicates that heat is released in this process.) From the reaction equation

$(C_6H_5)_2(s) + 19/2\ O_2(g) \rightarrow 12\ CO_2(g) + 5\ H_2O(l)$

we have $\Delta n_g = 12 - (19/2) = -5/2$. Substituting into Eq. 8 (Page 22), we have

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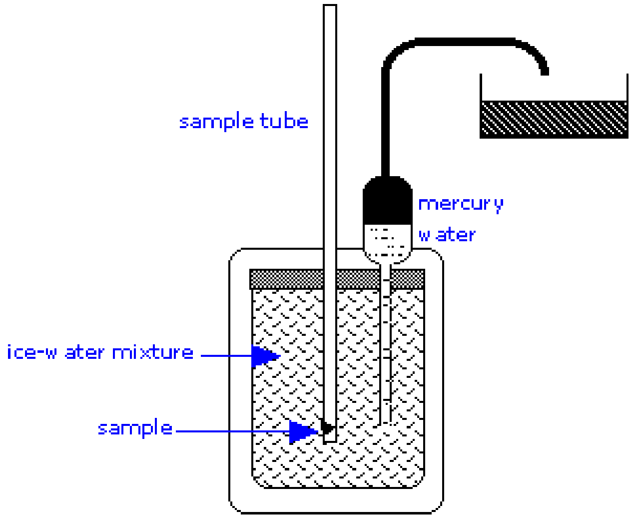
Although calorimetry is simple in principle, its practice is a highly exacting art, especially when applied to processes that take place slowly or involve very small heat changes, such as the germination of seeds.

Fig. 6: The ice calorimeter



The ice calorimeter is an important tool for measuring the heat capacities of liquids and solids, as well as the heats of certain reactions. This simple yet ingenious apparatus is essentially a device for measuring the change in volume due to melting of ice. To measure a heat capacity, a warm sample is placed in the inner compartment, which is surrounded by a mixture of ice and water. The heat withdrawn from the sample as it cools causes some of the ice to melt. Since ice is less dense than water, the volume of water in the insulated chamber decreases. This causes an equivalent volume of mercury to be sucked into the inner reservoir from the outside container. The loss in weight of this container gives the decrease in volume of the water, and thus the mass of ice melted. This, combined with the heat of fusion of ice, gives the quantity of heat lost by the sample as it cools to 0°C.

7 Some applications of First-law-related topics

7.1 Enthalpy diagrams

Comparison and interpretation of enthalpy changes is materially aided by a graphical construction in which the relative enthalpies of various substances are represented by horizontal lines on a vertical energy scale. The zero of the scale can be placed anywhere, since energies are always arbitrary anyway. An enthalpy diagram for carbon and oxygen and its two stable oxides is shown below. The labeled arrows show the changes in enthalpy associated with the various reactions this system can undergo. Notice how Hess' law is implicit in this diagram; we can calculate the enthalpy change for the combustion of carbon monoxide to carbon dioxide, for example, by subtraction of the appropriate arrow lengths without writing out the thermochemical equations in a formal way.

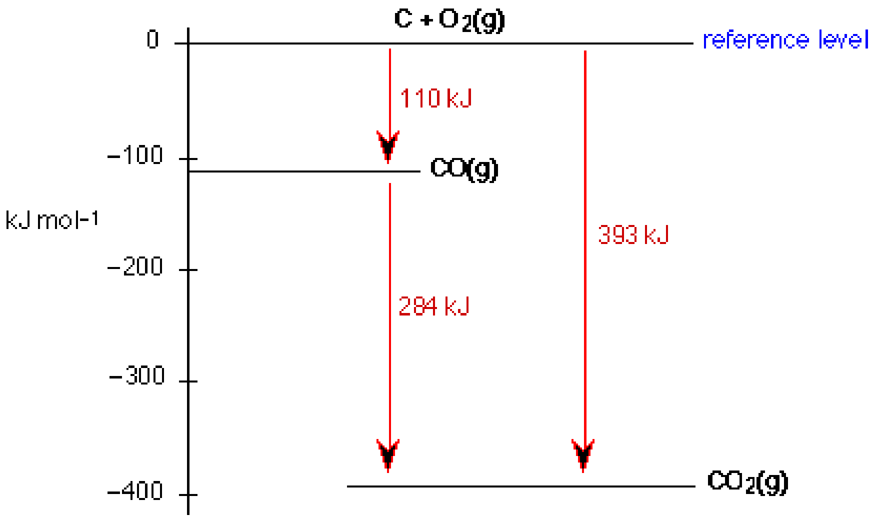


Fig. 7: Enthalpy diagram for the C-O system

In this diagram, we follow the convention of assigning zero enthalpy to graphite, the most stable state of the elements at 298 and 1 atm pressure. The labeled arrows show the changes in enthalpy associated with the various reactions this system can undergo. Notice how Hess' law is implicit in this diagram; we can calculate the enthalpy change for the combustion of carbon monoxide to carbon dioxide, for example, by subtraction of the appropriate arrow lengths without writing out the thermochemical equations in a formal way.

Enthalpy diagrams are especially useful for comparing groups of substances having some common feature. In the Figure below the molar enthalpies of species relating to two hydrogen halides are shown with respect to those of the elements. From this diagram we can see at a glance that the formation of HF from the elements is considerably more exothermic than is the corresponding formation of HCl. The upper part of this diagram shows the gaseous atoms at positive enthalpies with respect to the elements. The endothermic processes in which the H_2 and the dihalogen are dissociated into atoms can be imagined as taking place in two stages, also shown. From the enthalpy change associated with the dissociation of H_2 (218 kJ mol^{-1}), the dissociation enthalpies of F_2 and Cl_2 can be calculated and placed on the diagram.

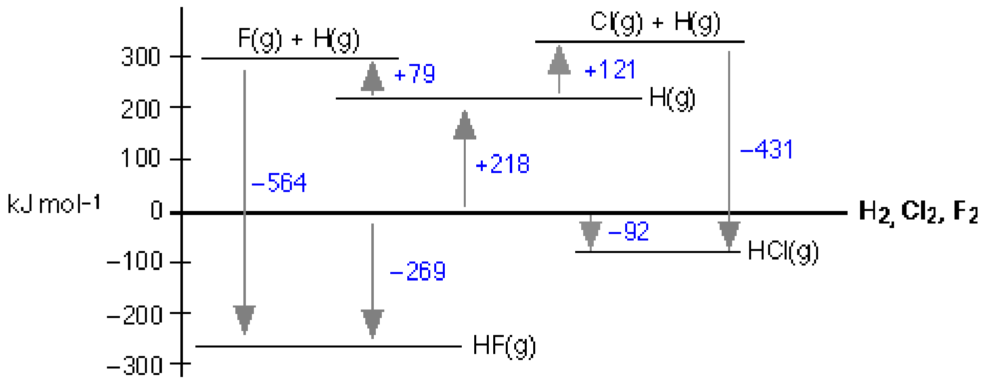


Fig. 8: Enthalpy diagram comparing HF and HCl

7.2 Bond enthalpies and bond energies

The energy change associated with the reaction

$$HI(g) \rightarrow H(g) + I(g)$$

is the heat of dissociation of the HI molecule; it is also the ***bond energy*** of the hydrogen-iodine bond in this molecule. Under the usual standard conditions, it would be expressed either as the bond enthalpy $H°_{HI(298)}$ or internal energy $U°_{HI(298)}$; in this case the two quantities differ from each other by $\Delta PV = RT$. Since this reaction cannot be studied directly, the H–I bond enthalpy is calculated from the appropriate standard enthalpies of formation:

$1/2\ H_2(g) \rightarrow H(g)$	+218 kJ
$1/2\ I_2(g) \rightarrow I(g)$	+107 kJ
$1/2\ H_2(g) + 1/2\ I_2(g) \rightarrow HI(g)$	–36 kJ
$\mathbf{HI(g) \rightarrow H(g) + I(g)}$	**+299 kJ**

Bond energies and enthalpies are important properties of chemical bonds, and it is very important to be able to estimate their values from other thermochemical data. The total bond enthalpy of a more complex molecule such as ethane can be found from the following combination of reactions:

$C_2H_6(g) \rightarrow 2C\ (graphite) + 3\ H_2(g)$	84.7 kJ
$3\ H_2(g) \rightarrow 6\ H(g)$	1308 kJ
$2\ C\ (graphite) \rightarrow 2\ C(g)$	1430 kJ
$\mathbf{C_2H_6(g) \rightarrow 2\ C(g) + 6H(g)}$	**2823 kJ**

Pauling's rule and average bond energy The total bond energy of a molecule can be thought of as the sum of the energies of the individual bonds. This principle, known as ***Pauling's Rule***, is only an approximation, because the energy of a given type of bond is not really a constant, but depends somewhat on the particular chemical environment of the two atoms. In other words, all we can really talk about is the *aver-*

age energy of a particular kind of bond, such as C–O, for example, the average being taken over a representative sample of compounds containing this type of bond, such as CO, CO_2, $COCl_2$, $(CH_3)_2CO$, CH_3COOH, etc.

Despite the lack of strict additivity of bond energies, Pauling's Rule is extremely useful because it allows one to estimate the heats of formation of compounds that have not been studied, or have not even been prepared. Thus in the foregoing example, if we know the enthalpies of the C–C and C–H bonds from other data, we could estimate the total bond enthalpy of ethane, and then work back to get some other quantity of interest, such as ethane's enthalpy of formation.

By assembling a large amount of experimental information of this kind, a consistent set of average bond energies can be obtained. The energies of double bonds are greater than those of single bonds, and those of triple bonds are higher still.

	H	C	N	O	F	Cl	Br	I	Si
H	436	415	390	464	569	432	370	295	395
C		345	290	350	439	330	275	240	360
N			160	200	270	200	245		
O				140	185	205	220	200	370
F					160	255	235	280	540
Cl						243	220	210	359
Br							190	180	290
I								150	210
Si									230

Table 6: Average energies of some single bonds (kJ/mol)

7.3 Energy content of fuels

A fuel is any substance capable of providing useful amounts of heat through a process that can be carried out in a controlled manner at economical cost. For most practical fuels, the process is *combustion* in air (in which the oxidizing agent O_2 is available at zero cost.) The *enthalpy of combustion* is obviously an important criterion for a substance's suitability as a fuel, but it is not the only one; a useful fuel must also be easily ignited, and in the case of a fuel intended for self-powered vehicles, its *energy density* in terms of both mass (kJ kg^{-1}) and volume (kJ m^{-3}) must be reasonably large. Thus substances such as methane and propane which are gases at 1 atm must be stored as pressurized liquids for transportation and portable applications.

fuel	MJ kg^{-1}
wood (dry)	15
coal (poor)	15
coal (premium)	27
ethanol[a]	30
petroleum products	45
methane	54
hydrogen[b]	140

Table 7: energy density of some common fuels

Notes on the above table:

a) **Ethanol** is being strongly promoted as a motor fuel by the U.S. agricultural industry. Note, however, that it takes 46 MJ of energy to produce 1 kg of ethanol from corn.

b) Owing to its low molar mass and high heat of combustion, **hydrogen** possesses an extraordinarily high energy density, and would be an ideal fuel if its critical temperature (33 K, the temperature above which it cannot exist as a liquid) were not so low. The potential benefits of using hydrogen as a fuel have motivated a great deal of research into other methods of getting a large amount of H_2 into a small volume of space. Simply compressing the gas to a very high pressure is not practical because the weight of the heavy-walled steel vessel required to withstand the pressure would increase the effective weight of the fuel to an unacceptably large value. One scheme that has shown some promise exploits the ability of H_2 to "dissolve" in certain transition metals. The hydrogen can be recovered from the resulting solid solution (actually a loosely-bound compound) by heating.

7.4 Energy content of foods

What, exactly, is meant by the statement that a particular food "contains 1200 calories" per serving? This simply refers to the standard enthalpy of combustion of the foodstuff, as measured in a bomb calorimeter. Note, however, that in nutritional usage, the calorie is really a kilocalorie (sometimes called "large calorie"), that is, 4184 J. Although this unit is still employed in the popular literature, the SI unit is now commonly used in the scientific and clinical literature, in which energy contents of foods are usually quoted in kJ per unit of weight.

Although the mechanisms of oxidation of a carbohydrate such as glucose to carbon dioxide and water in a bomb calorimeter and in the body are complex and entirely different, the net reaction involves the same initial and final states, and must be the same for any possible pathway.

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \qquad \Delta H° – 20.8\ \text{kJ mol}^{-1}$$

Glucose is a sugar, a breakdown product of starch, and is the most important energy source at the cellular level; fats, proteins, and other sugars are readily converted to glucose. By writing balanced equations for the combustion of sugars, fats, and proteins, a comparison of their relative energy contents can be made. The stoichiometry of each reaction gives the amounts of oxygen taken up and released when a given amount of each kind of food is oxidized; these gas volumes are often taken as indirect measures of energy consumption and metabolic activity; a commonly-accepted value that seems to apply to a variety of food sources is 20.1 J (4.8 kcal) per liter of O_2 consumed.

For some components of food, particularly proteins, oxidation may not always be complete in the body, so the energy that is actually available will be smaller than that given by the heat of combustion. Mammals, for example, are unable to break down cellulose (a polymer of sugar) at all; animals that derive a major part of their nutrition from grass and leaves must rely on the action of symbiotic bacteria which colonize their digestive tracts. The amount of energy available from a food can be found by measuring the heat of combustion of the waste products excreted by an organism that has been restricted to a controlled diet, and subtracting this from the heat of combustion of the food.

type of food	food	$\Delta H°_{\text{combustion}}$, kJ g^{-1}	percent availability
Protein	meat	22.4	92
	egg	23.4	
Fat	butter	38.2	
	animal fat	39.2	95
Carbohydrate	starch	17.2	
	glucose (sugar)	15.5	99
	ethanol	29.7	100

Table 8: Energy content and availability of the major food components

The amount of energy an animal requires depends on the age, sex, surface area of the body, and of course on the amount of physical activity. The rate at which energy is expended is expressed in *watts*: 1 W = 1 J sec^{-1}. For humans, this value varies from about 200-800 W. This translates into daily food intakes having energy equivalents of about 10-15 MJ for most working adults. In order to just maintain weight in the absence of any physical activity, about 6 MJ per day is required.

animal	kJ hr^{-1}	kJ kg^{-1} hr^{-1}
mouse	.82	17
cat	34	6.8
dog	78	3.3
sheep	193	2.2
man	300	2.1
horse	1430	1.1
elephant	5380	0.7

Table 9: metabolic rates of some mammals

The above table is instructive in that although larger animals consume more energy, the energy consumption per unit of body weight decreases with size. This reflects the fact that many metabolic functions, as well as heat loss, depend directly or indirectly on the surface area of the body. The ratio of surface area to mass is of course greater for smaller animals.

7.5 Thermodynamics and the weather

Hydrogen bonds at work It is common knowledge that large bodies of water have a “moderating” effect on the local weather, reducing the extremes of temperature that occur in other areas. Water temperatures change much more slowly than do those of soil, rock, and vegetation, and this effect tends to affect nearby land masses. This is largely due to the high heat capacity of water in relation to that of land surfaces— and thus ultimately to the effects of hydrogen bonding. The lower efficiency of water as an absorber and radiator of infrared energy also plays a role.

Sea breezes and land breezes

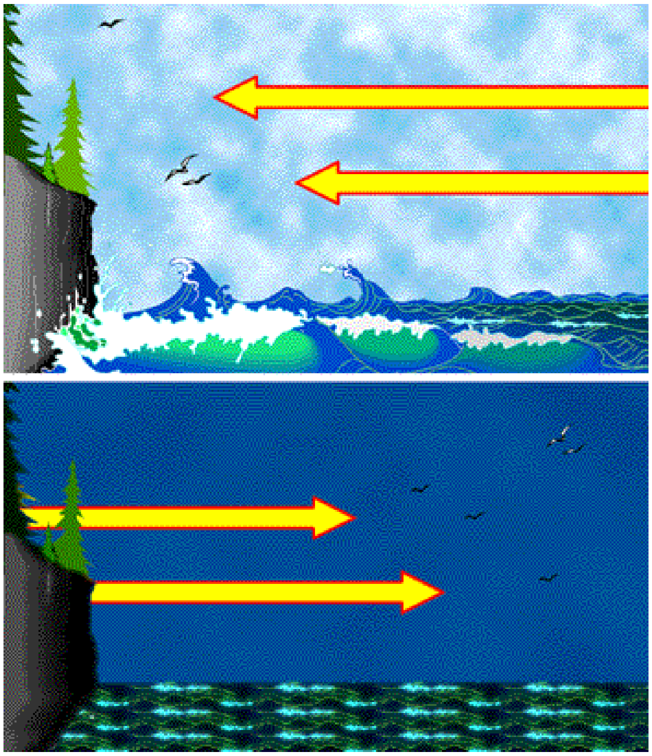


Fig. 10: Land breezes and sea breezes

The specific heat capacity of water is about four times greater than that of soil. This has a direct consequence to anyone who lives near the ocean and is familiar with the daily variations in the direction of the winds between the land and the water. Even large lakes can exert a moderating influence on the local weather due to water's relative insensitivity to temperature change.

During the daytime the land and sea receive approximately equal amounts of heat from the Sun, but the much smaller heat capacity of the land causes its temperature to rise more rapidly. This causes the air above the land to heat, reducing its density and causing it to rise. Cooler oceanic air is drawn in to vill the void, thus giving rise to the daytime sea breeze.

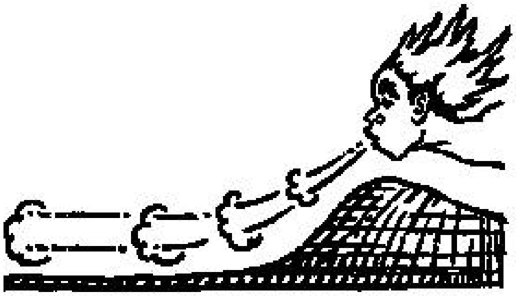
In the evening, both land and ocean lose heat by radiation to the sky, but the temperature of the water drops less than that of the land, continuing to supply heat to the oceanic air and causing it to rise, thus reversing the direction of air flow and producing the evening land breeze.

(The image is from the Web site of the National Data Buoy Center)

Why it gets colder as you go higher: the adiabatic lapse rate

The air receives its heat by absorbing far-infrared radiation from the earth, which of course receives its heat from the sun. The amount of heat radiated to the air immediately above the surface varies with what's on it (forest, fields, water, buildings) and of course on the time and season. When a parcel of air above a particular location happens to be warmed more than the air immediately surrounding it, this air expands and becomes less dense. It therefore rises up through the surrounding air and undergoes further expansion as it encounters lower pressures at greater altitudes. Whenever a gas expands against an opposing pressure, it does work on the surroundings. According to the First Law $\Delta U = q + w$, if this work is not accompanied by a compensating flow of heat into the system, its internal energy will fall, and so, therefore, will its temperature. It turns out that heat flow and mixing are rather slow processes in the atmosphere in comparison to the convective motion we are describing, so the First Law can be written as $\Delta U = w$ (recall that w is negative when a gas expands.) Thus as air rises above the surface of the earth it undergoes adiabatic expansion and cools. The actual rate of temperature decrease with altitude depends on the composition of the air (the main variable being its moisture content) and on its heat capacity. For dry air, this results in an adiabatic lapse rate of 9.8 C° per km of altitude.

Santa Anas and chinooks: those warm, wild winds



Just the opposite happens when winds develop in high-altitude areas and head downhill. As the air descends, it undergoes compression from the pressure of the air above it. The surroundings are now doing work on the system, and because the process occurs to rapidly for the increased internal energy to be removed as heat, the compression is approximately adiabatic. The resulting winds are warm (and therefore dry) and are often very irritating to mucous membranes. These are known generically as *Föhn* winds (which is also the name given to those that originate in the Alps.) In North America they are often called *chinooks* (or, in winter, "snow melters") when they originate along the Rocky Mountains. Among the most notorious are the *Santa Ana* winds of Southern California which pick up extra heat (and dust) as they pass over the Mohave Desert before plunging down into the Los Angeles basin.