Chapter 19: Work, Heat, & the 1st Law of Thermodynamics

Let me summarize where I am going with this first. In Phys 4A, we found that in mechanical systems KE is not a conserved quantity of nature, as well as PE. However, the combination of KE + PE (= constant) is a conserved quantity. In thermodynamic processes, a similar thing occurs: work and heat are not conserved quantities of nature but the quantity Work – Heat (= constant) is conserved. The conceptual and mathematical power of conservation of energy made analyzing and solving problem considerably easier. We will apply the same type of thinking to thermodynamic system too.

A key idea of energy is the work-energy theorem:

\[ W_{\text{net}} = W_{\text{C}} + W_{\text{NC}} + W_{\text{ext}} = \Delta K \]

This tells us that the net work done on a system of particles will change its KE when forces do work on the particles by pushing or pulling them through a distance.

1. Work done by conservative forces changes the system’s PE: \( W_{\text{C}} = -\Delta U_{\text{macro}} \)
2. Work done by friction \( W_{\text{NC}} \) increases the system’s thermal energy but decreases the available energy of the system: \( W_{\text{NC}} = -\Delta E_{\text{th}} \)
3. Work done by external forces \( W_{\text{ext}} \) (originates in the environment) increases the system’s energy: \( W_{\text{ext}} = +\Delta E_{\text{system}} \).

Rewriting the work-energy theorem in this language leads to

\[ W_{\text{ext}} = \Delta K + \Delta U_{\text{macro}} + \Delta E_{\text{th}} = \Delta E_{\text{system}} \]

Definitions

- The macroscopic energies of a system associated with the motion as a whole is defined as \( E_{\text{mech}} = K + U \) (this is the energy you were taught in Phys 4A).
- The microscopic energies within the system is called the internal energy, that’s the energy inside the object (or thermal energy) where \( E_{\text{int}} \equiv E_{\text{th}} \equiv K_{\text{micro}} + U_{\text{micro}} \) and is associated with the KE and PE of the atoms and molecules.

Example: suppose my system is composed of a car, the air and the road. The moving car has both macroscopic energies and microscopic energies (the atoms and spring-like molecular bonds of the car, the air and the road).

There is a problem with conservation of energy as seen in Phys 4A – it’s incomplete. Why? Standard conservation of energy emphasized isolated systems from the environment. When this is true, then \( W_{\text{ext}} = 0 = \Delta E_{\text{system}} \) (i.e. \( K_1 + U_1 = K_2 + U_2 \)). That is, there was no transfer of energy between the system and the environment. However, in reality, the environment plays a huge role in systems. To make conservation of energy more complete, we will need to focus on how energy is transferred between the system and its environment. Our immediate goal is to write the complete form of conservation of energy. When focusing on thermodynamics, there is a name change from conservation energy to the first law of thermodynamics, which focuses instead only on the microstates (or internal energies) of the system.

Internal Energies (\( E_{\text{micro}} \equiv E_{\text{int}} \)): KE & PE at the Microscopic Level

All of the objects that we handle in everyday situations contain vast numbers of atoms internally. There are two perspectives:

i. Macrophysics is a system view of a “large” object moving with both KE and PE: \( K_{\text{macro}} = m_{\text{obj}} v_{\text{obj}}^2 \) and \( U_{\text{macro}} = m_{\text{obj}} g y \). As you will see, we will ignore both \( K_{\text{macro}} \) and \( U_{\text{macro}} \) immediately since they play no significant role in microphysics.

ii. Microphysics is a collection of atoms/molecules such that each of the atoms store both KE and PE. Using the spring model of atoms, atoms have KE that in turn stretch out tiny electrical springs that store electrical PE (or bond energy). Although the amount of energy of a single atom is exceedingly small, atoms
are so numerous that it is beyond imagination. Once again, the total microscopic KE and PE are defined as the internal energy of the system: \( E_{\text{int}} = K_{\text{micro}} + U_{\text{micro}} \).

**Is the microscopic energy worth worrying about?**

**Example**

Consider a 500 g (\(\approx 1\) lb) iron ball moving with speed 20 m/s (\(\approx 45\) mph) along a flat surface (\(\Delta U_{\text{macro}} = 0\)). Its macroscopic energy (\(= K_{\text{macro}}\)) is

\[
E_{\text{macro}} = K_{\text{macro}} = \frac{1}{2} m_{\text{obj}} v_{\text{obj}}^2 = \frac{1}{2} \cdot 0.500 \cdot 20^2 = 100 J = E_{\text{macro}}
\]

On the other hand, the mass of an iron ball is composed of numerous iron atoms where

\[
N_{\text{iron atoms}} \approx 10^{25} \quad \text{and} \quad m_{\text{iron atom}} \approx 10^{-20} \text{kg}
\]

Atoms move faster in solids than they do in air (340 m/s), and a rough estimate is 500 m/s. The KE of a single atom is tiny but \(K_{\text{micro}}\) is surprisingly large:

\[
K_{\text{atom}} = \frac{1}{2} m v^2 = \frac{1}{2} \cdot 10^{-25} \text{kg} \cdot 500^2 \approx 10^{-20} \text{ J}
\]

but the total microscopic \(K_{\text{micro}}\) is surprisingly large:

\[
K_{\text{micro}} \approx N K_{\text{atom}} = 10^{25} \cdot \cdot 10^{-20} \text{ J} \approx 100,000 \text{ J}
\]

From our “studies of spring motion”, the maximum energy stored in the spring is on average \(U_{\text{micro}} \approx K_{\text{micro}}\), so

\[
E_{\text{micro}} = K_{\text{micro}} + U_{\text{micro}} \approx 2 K_{\text{micro}} \approx 200,000 \text{ J} = E_{\text{micro}}
\]

Clearly,

\[
\frac{E_{\text{micro}}}{E_{\text{macro}}} \approx \frac{200,000 \text{ J}}{100 \text{ J}} \approx 2000 \rightarrow E_{\text{micro}} \gg E_{\text{macro}}
\]

It should come as a surprise that the microscopic energy content is higher than the macroscopic energy content. You can now see why conservation of energy via Phys 4A is incomplete.

It is clear now that microscopic energy is clearly hidden from our macrophysics perspective, but it is quite real. We will discover later that the **internal energy is proportional to the temperature of the system**. Raising the temperature causes the atoms to move faster and the bonds to stretch more, giving the system more internal energy. Now let's deal with the “heat”. The word “heat” is like the word “work”. Work has a narrow and precise meaning in physics that is much more restricted than its use in everyday language. We will introduce the concept of heat later, when we need it. For the time being we want to use the correct term: “thermal or internal energy” is the description of the random motion of atoms that stores both KE and PE in a system internally. Strictly speaking, the “thermal” energy is only one form of the microscopic energy that can be stored, there is also chemical, nuclear…:

\[
E_{\text{int}} = E_{\text{in}} + E_{\text{chem}} + E_{\text{nuclear}} + \cdots
\]

The total energy of the system is then \(E_{\text{system}} = E_{\text{mech}} + E_{\text{int}}\). For this course, when we say the word thermodynamics we solely concentrate on the microscopic energies of the system and leave other forms of internal energy to more advanced courses.

**Only changes in energy are meaningful: Energy Transfer**

Since we have neglected the environment for conservation of energy, how does the environment change the energy of the system? In other words, how is energy transferred from one energy state to another energy state?

- If a block is being lifted by a rope at constant velocity, the rope’s tension does work and this work changes the energy state of the block. That is, there is an energy transfer (usually called work) that increases the system’s macroscopic PE \((U_g)\): \(W_{\text{ext}} = \Delta E_{\text{mech}}\).

- If the same rope (and same tension) drags the object at constant velocity across a rough surface, the work done by friction increases the thermal or internal energy of the system: \(W_{\text{ext}} = \Delta E_{\text{int}} \equiv \Delta E_{\text{ent}}\). Note that this does
NOT increase the \( E_{\text{mech}} \) of the system. The point here is that the energy transferred to a system can go either into entirely the system’s \( E_{\text{mech}} \), into \( E_{\text{th}} \), or some combination of the two. The energy isn’t lost, but where it ends up depends on the circumstances. Here is the core problem with conservation of energy from a Phys 4A perspective.

You can transfer energy into a system by a **MECHANICAL INTERACTION** by doing work. However, if I heat a pan of water on the stove, the water temperature increases so its thermal/internal energy increases, which we write as \( \Delta E_{\text{th}} \equiv \Delta E_{\text{int}} > 0 \). But from a Phys 4A viewpoint, no work is done and therefore, there is no change in the water’s mechanical energy (\( W_{\text{ext}} = E_{\text{mech}} = 0 \)). But clearly this is not correct since there is an increase in the internal energy of the system, even though no work was done. So, something is wrong? Clearly, the energy equation, as it stands, is incomplete.

**Adding Heat as a form of energy transfer**

Work is an energy transfer process in a mechanical interaction, which we call working. As we have just seen, this is **NOT** the only way a system can interact with its environment. Energy can also be transferred between the system and the environment if there is a **THERMAL INTERACTION** where this interaction is called heat or heating \( \equiv Q \). When heat is included, the complete statement of the work-energy theorem (conservation of energy) is

\[
\Delta E_{\text{system}} = \Delta E_{\text{macro}} + \Delta E_{\text{micro}} = Q + W
\]

In other words, heat was the missing piece to the complete principle of conservation of energy. **Work and heat are two ways of transferring energy between a system and the environment and causes the system’s energy to change.**

Since this part of the course is on thermodynamic systems, we will not be interested in the macroscopic motion of the system and ignore \( \Delta E_{\text{macro}} \) and only focus on \( \Delta E_{\text{micro}} \equiv \Delta E_{\text{int}} \). To drive this point clearly, consider the following example: if we boil a pot of water to make pasta, we want the pot as a whole to rest peacefully on the stove while we study it (i.e. the macroscopic energy of the system does not change (\( \Delta E_{\text{mech}} = 0 \)) but clearly its internal energy changes (\( \Delta E_{\text{int}} \neq 0 \)). The first law of thermodynamics reads

\[
\Delta E_{\text{micro}} \equiv \Delta E_{\text{int}} = \frac{Q + W}{\text{cause of a change in internal energy}}
\]

Unfortunately, things are not so simple: there are two conventions in how work is defined for a system and appears in two different ways:

\[
\Delta E_{\text{th}} = \begin{cases} 
Q + W & \text{IUPAC convention (modern one)} \\
Q - W & \text{Clausius convention (old one)} 
\end{cases}
\]

**Which form of the first law of thermodynamics should I use?**

In the course, I plan on using the IUPAC convention so that the **First Law of Thermodynamics** reads as

\[
\Delta E_{\text{int}} = \Delta E_{\text{th}} = Q + W
\]

The first law is so important that it sets the framework of how we solve all problems in chapters 18, 19 and 20. To understand this framework, we need to define (1) State Variables and the State Equation (which we did in chapter 18), (2) Work, (3) Heat, and putting it altogether in (4) the First Law of Thermodynamics.
In summary, a mechanical or thermal interaction changes the internal energy of system from state-1 to state-2, and we measure this change by measuring the changes in the state variables.

As I have already stated, the word heat is a “slippery” concept and misused frequently. **Work and heat are not state variables** since they are a catalyst to change the internal energy of the system. Note also that we can measure the change in a state variable (ΔT, Δp or ΔV), but it makes no sense to talk about a “change in work” or “change in heat.” Consequently, work always appears as W, never as ΔW; similarly, heat always appears as Q, not ΔQ!

Before I get started on defining thermodynamic working and heating, all thermodynamics processes (sometimes called paths) must be carried out in a **quasi-equilibrium (or quasi-static)** manner. A thermodynamic process takes a state (state-1) to another state (state-2), the system is in a state of transition. This transitional state must be quasi-equilibrium. **What is quasi-equilibrium (or quasi-static)?**

**Analogy:** suppose you were to walk to Safeway to get a sandwich. In order to walk there, you are clearly taking one small step at a time. Each of these steps are “infinitesimal in size” compared to the overall distance to Safeway. However, from a helicopter’s viewpoint, you would appear to be essentially moving very very slowly and in a state of “quasi-equilibrium.” In other words, your current step did not move you very far from your previous step and therefore, you are essentially in a state of almost equilibrium from your previous step.

A similar process occurs in thermodynamics. When a system changes from state-1 to state-2, it passes through a series of intermediate states in a quasi-equilibrium manner. For example, when the pressure changes, the pressure only changes by an infinitesimal amount \( p_1 + \Delta p = p_2 \) where \( \Delta p \) is infinitely small. The whole collection of quasi-equilibrium states is called a **THERMODYNAMIC PATH (or path)** and plotted on a pV-diagram.

1. **WORKING:** any work interaction requires a macroscopic change in the motion of the system (i.e., a change in volume), where we assume \( Q = 0 \) for simplicity. Picture-wise, I draw the following mechanical analogy:

   ![Mechanical Analogy](image)

   **The sign of Work**
   The definition of the Clausius convention determines the sign convention used for work. Focusing only on mechanical interactions only (\( Q = 0 \)), changes in internal energy is equal to the negative of the work:
   \[
   \Delta E_{\text{int}} = Q + W = +W
   \]
   How does one interpret the meaning of the minus sign? A common example of a thermodynamic system is a gas enclosed in a cylinder with a movable piston.
DEMO Pasco piston

I assume you have been introduced to pressure in either Phys 11 (or in high school physics):

\[
\text{pressure} = \frac{\text{Force}}{\text{Area}} \rightarrow p = \frac{F}{A}
\]

We can rewrite the mechanical work expression in terms of the state variables of \( p \) and \( V \):

\[
dW = Fdx = p(Adx) = pdV \rightarrow W = \int_{x_1}^{x_2} Fdx = \int_{V_1}^{V_2} pdV
\]

However, thermodynamic work is redefined under the first law and reads as

\[
W = -\int_{V_1}^{V_2} pdV \equiv \text{negative area under the curve pV-diagram}
\]

We now consider the work done by a piston by either compressing or expanding and asked how are the motions of the gas molecules changing?

Compressing a piston (decreasing volume)

When a piston is compressed, there is a decrease in volume since \( V_2 < V_1 \). Physically, what happens to the gas molecules during the compression? Image a single gas molecule moving towards the piston wall and colliding with it. By the impulse-momentum theorem, the gas molecule after the collision must speed up and gain KE. In other words, the work of the piston transferred its "work" to the gas molecules and increased their KE. In the language of thermodynamics, we measure a change in the state variables (decreased volume implies a higher pressure and temperature) and therefore, the internal energy of the system has increased through a mechanical interaction. Work is done ON the gas when the volume decreases and increases the \( \Delta E_{\text{int}} \) of the gas.

\[
\Delta V < 0 \quad \rightarrow \quad W > 0 \quad \rightarrow \quad \Delta E_{\text{int}} > 0
\]

In summary,

\[
\Delta E_{\text{int}} = +W \rightarrow E_{\text{int},1} + W = E_{\text{int},2}
\]

Expanding a piston (increasing volume)

Physically, what happens to the gas molecules during an expansion? If the speed of a single molecule is moving fast enough towards the piston wall and the piston wall expands, then the gas molecule after the collision must have slowed down and loses KE. In other words, it is the gas molecules that transferred its "work" to the piston walls which decreased their KE. In the language of thermodynamics, we measure a change in the state variables (increased volume but a lower pressure and temperature) and therefore, the internal energy of the system has decreased through a mechanical interaction. Work is done BY the gas when the volume increases and decreases the \( \Delta E_{\text{int}} \) of the gas.

\[
\Delta V > 0 \quad \rightarrow \quad W < 0 \quad \rightarrow \quad \Delta E_{\text{int}} < 0
\]
\[ \Delta E_{\text{int}} = -W \rightarrow E_{\text{int,1}} - W = E_{\text{int,2}} \]

**Question:** Is \( pV \) energy part of the internal energy \( U_{\text{int}} \)?

**Answer:** \( pV \) should not be included as part of the internal energy of the system. It is the energy required to make a system. Of course, we need to supply the energy \( U_{\text{int}} = K_{\text{micro}} \), which involves things like the motion of the particles (or any potential energies), but we also need to make room for this system. In order to do this, we must push the atmosphere or whatever surrounding gas out of the way. This is where the \( pV \) term comes in. It is not involved in the internal energy \( U_{\text{int}} \). Note that \( p \) here is not the pressure within the system in question. Since we are talking about pushing whatever gas is present out of the way, \( p \) is the pressure of the surrounding atmosphere that the system is in. This is why it is not included as part of the internal energy.

**Work is Path Dependent**

Processes are either path independent (these are conservative forces) or path dependent (nonconservative forces). Thermodynamic processes have nonconservative forces doing work and are therefore, path dependent.

**Example:** consider the following two ways to go from state-1 to state-2 by doing work: \( 1 \rightarrow 3 \rightarrow 2 \) or \( 1 \rightarrow 4 \rightarrow 2 \). In thermodynamic processes, the order of operation matters a lot. If we take the path \( 1 \rightarrow 3 \rightarrow 2 \), we see that we start with a constant pressure process and end with a constant volume process. On the other hand, path \( 1 \rightarrow 4 \rightarrow 2 \) starts with a constant volume process and ends with a constant pressure process. Even though we start and end at the same points, the amount of workings in each case are quite different. It is clear that path \( 1 \rightarrow 3 \rightarrow 2 \) has a larger area than path \( 1 \rightarrow 4 \rightarrow 2 \), so the order of operation is clearly important and gives different results. In other words, the fact that \( W(1 \rightarrow 3 \rightarrow 2) \neq W(1 \rightarrow 4 \rightarrow 2) \) implies that work is path dependent and is not a conserved quantity in thermodynamic processes.

2. **HEATING:** any heat interaction requires a microscopic change in the motion of the system (atoms move faster or slower), where we assume \( W = 0 \) for simplicity.

Heat is a more elusive concept than work. We use the word “heat” very loosely in the English language, often as synonymous with hot. We might say on a very hot day, “this heat is oppressive.” If your apartment is cold, you may say, “turn up the heat.” These expressions date to a time long ago when it was thought that heat was a substance with fluid-like properties. Heat is not a substance. For example, a hot apple pie does not contain heat even though it is hot.

The first person to recognize it clearly was Joule (1840). He found that you can raise the temperature of a beaker of water by two entirely different means:

i. Heat it with a flame, or
ii. Doing work on it with a rapidly spinning paddle wheel.

If the initial and final temperatures of the water are exactly the same in both cases, this implies that heat and work are on the same footing. Heating and working are two different ways of changing the internal energy. To be specific, **HEAT** is the energy transferred between the environment and the system that either increases or decreases the microscopic motions of the system.

That is, thermal interactions either increase the internal energy \( (Q > 0) \) or decrease it \( (Q < 0) \). To see this, we need to speak about the increase or decrease in the microscopic motions of the atoms/molecules. Suppose heat is transferred and there is a **temperature change** to the system. What does this mean?
Increasing internal energy and temperature
Suppose that you place a pot of water onto a stove that you plan on bringing to a boil. What happens when a flame interacts with the metal pot from the molecular level?

DEMO spring model
The flame essentially sends in fast moving gas molecules that collide with a large spring system of metal atoms. The first metal atoms are “excited” and are accelerated, which in turn start to excite the next layer of metal atoms and the process continues on. These collisions create a “ripple affect” through the metal pot that end up all juggling around in excited states. As the internal energy increases, the more KE and PE in stored in metal atoms. (This heat transfer process is called conduction from an atomic level viewpoint.) We are not interested in the pot, we are interested in the water so let’s focus on this. A similar process occurs between the hot metal pot and the cool water molecules. The heat transferred from the flames ($Q > 0$) excited metal atoms, which in turn collide with slower, cooler water molecules and speed them, which gain energy. Therefore, heat transferred in ($Q > 0$) increased the overall internal energy ($\Delta E_{\text{int}} > 0$) in the system.

Question, do the hotter metal atoms slow down? Yes; so, their internal energy decreases. So why doesn’t the pot cool off? It doesn’t cool off because the flame is consisting supplying addition energy to re-energize the metal atoms in the pot.

$$\Delta E_{\text{int}} = Q$$

Decreasing internal energy and temperature
When faster moving molecules (in a hotter object) collide with slower moving molecules (in a cooler object) in the system, the faster molecules lose energy and thus the overall internal energy decreases ($\Delta E_{\text{int}} < 0$) in the system.

Focus on Heat only (not work $W = 0$)
If we focus only on changing the internal energy by heating ($W = 0$), then we write

$$\Delta E_{\text{int}} = Q$$

Like work, the heat added to a thermodynamic system is path dependent because nonconservative forces are at work. In thermodynamics, we call this “not reversible.”

Heat is path dependent $\rightarrow$ not conserved in any thermo processes

Example: Suppose we want to change the volume of a certain quantity of an ideal gas from 2.0 to 5.0 L while keeping the temperature constant at $T = 300$ K. There are two different ways in which we can do this and reach the same final state.

Heat Path-1 (isothermal = constant temperature)

The gas contained in the piston starts with an initial volume of 2.0 L. Let’s physically think this through: (i) If the volume of the piston expands to 5.0 L, the number of collisions in the gas decreases, so there is a decrease in internal energy and the temperature decreases. (ii) To keep the temperature constant, the average KE has to increase for the gas molecules. As already discussed, we transfer heat from the hot metal bottom of the piston, which in turn, excites the gas molecules and increases their overall average KE.
Heat Path-2 (free expansion in an insulated container)

Suppose that the piston is now surrounded by insulating walls so that no energy is allowed to leak out (think of a tea thermos). Inside the piston there is a thin, breakable partition at the 2.0 L mark in a 5.0 L piston volume. If the gas in the 2.0 L compartment has an initial temperature of 300 K and I now “push a button” that breaks this partition, the gas undergoes a rapid, uncontrolled expansion, with no heat passing through the insulating walls. The final volume is 5.0 L. The gas does no work during this expansion because it doesn’t push against anything that moves. This uncontrolled expansion of a gas into the vacuum is called a free expansion with no temperature change.

Here are two situations where the initial and final states in each situation end up being equal but these were achieved by two different heating processes. In other words, heat is path dependent and is not conserved in thermodynamic processes!

The First Law of Thermodynamics

Ignoring the macrophysics of conservation of energy, adding heat lead us to

\[
\Delta E_{\text{int}} = Q + W
\]

(first law of thermodynamics)

Remarks

1. Analogy: Mechanical energy in Phys 4A

KE and PE are not conserved quantities because they are path dependent:

\[
W = \Delta K \text{ or } K_1 + W = K_2 \rightarrow \begin{cases} K_1 \rightarrow \text{Work} \rightarrow K_2 \\ K_1 \neq K_2 \end{cases}
\]

Even though K and U are not conserved. KE and PE are path dependent. In a similar fashion, work W and heat Q is not conserved in different processes, we say in thermodynamics that these quantities are path dependent. However, the total energy \( \Delta E_{\text{int}} = Q + W \) is conserved and therefore, path independent

2. Conservation of energy doesn’t tell you anything about K or U, it sets up the underlying structure of how the system will change. You need other equations to tell you about them. In a very similar way, the first law sets the underlying structure of thermodynamic processes, which is why I introduced the 1st law first. Because it is the most important analytical tool we have to solving energy problems. The work and heat equations will have to be calculated by other means (similar K and U in mechanics).

3. The first law doesn’t tell us anything about the value of \( E_{\text{int}} \), only how \( E_{\text{int}} \) changes. Doing 1 J of work changes the internal energy by \( \Delta E_{\text{int}} = 1 \) J regardless of whether \( E_{\text{int}} = 10 \) J or 10,000 J.

4. The system’s internal energy isn’t the only thing that changes. Work or heat that changes the internal energy also changes the (p, V, T) and other state variables. The first law tells us only about \( \Delta E_{\text{int}} \). Other laws and relationships must be used to learn how the other state variables change.

5. The first law is one of the most important analytic tools of thermodynamics. We’ll use the first law in the remainder chapters to study the thermal properties of matter.

Sign Convention for Q, W and \( \Delta E_{\text{int}} \)

Because W and Q may be positive, negative, or zero, \( \Delta E_{\text{int}} \) can be positive, negative, or zero for different processes.
Interpretation of $\Delta E_{\text{int}} = Q + W$

The simple combination of heat plus work ($Q + W$) for each of the paths from the initial to the final state of the system is a constant—it remains the same for all of the processes. In addition, the quantity $Q + W$ depends only on the two states of the system: its initial and final states. This means that $Q + W$ must represent a change in an intrinsic property of the system. Because it only depends on the initial and final states, it is a state property. It turns out that this quantity, this change in a system’s intrinsic property, is defined as the internal energy of the system ($U_{\text{int}}$), which is a quantity that measures the capacity to induce a change that would not otherwise occur. It is associated with atomic and molecular motion and interactions. Degrees of freedom are the ways in which the atoms and molecules that make up a system can move around. The internal energy is the energy that is distributed over these different movements. Internal energy allows us to describe the changes that occur in a system for any type of energy transfer, whether from heat or work. And those energy transfers are exactly what the first law of thermodynamics keeps track of.

The first law of thermodynamics states the energy conservation principle: Energy cannot be created nor destroyed, but only converted from one form to another. Energy lost from a system is not destroyed; it is passed to its surroundings. The first law of thermodynamics is simply a statement of this conservation.

Example
The first law of thermodynamics can be thought of as a statement of energy conservation, but it is also a statement of the equivalence of work and heat. The first law says that you could change the internal energy of a system by some amount in two entirely different ways. Suppose that the internal energy of a system, $U$, is increased by 5 joules during some process. So, $\Delta U = 5$ joules. This could be accomplished by performing 5 joules of work on the system with no heat transfer at the boundaries of the system. In this case, $Q = 0$, and $\Delta U = Q + W = 0 + 5 = 5$ joules. (This type of process—where no heat is allowed to enter or leave the system, so $Q = 0$—is referred to as an adiabatic process.) On the other hand, you could transfer 5 joules of heat into the system while performing no mechanical work, or any other work for that matter. In this case, the process is non-adiabatic, and $W = 0$. In addition, $\Delta U = Q + W = 5 + 0 = 5$ joules. This simple example shows how both work and heat can be used to cause the same changes to the internal degrees of freedom of a system. Combining knowledge of the types of processes occurring with the first law allows you to calculate changes in internal energy directly from measurable quantities like heat and work.

It’s called a state variable when it doesn’t depend on the path taken. That brings us to the two energy transfer terms of the first law: work and heat, or $W$ and $Q$. In this case, we have variables that are not state variables, but rather, they are path dependent. That’s why we use a different differential to describe a change in such a variable. The $\delta$ is also called an inexact differential because if we integrate over it, we must specify a path for the integral. That makes sense if you think about it: We cannot integrate over a path-dependent variable without knowing its path. The $\delta$ is just our mathematical notation to make sure that we know what type of variable we’re describing. The first law states that for a given process, any change in $U$, the internal energy of the system, is equal to the sum of the energy transfer terms $Q$ and $W$. But now let’s write the first law in its differential form: The differential $dU$ equals the differential change in the internal energy of the system, which equals $dQ + dW$. Notice that for $U$, we use the exact differential ($d$)—that’s because internal energy is a state function and does not depend on the path taken, only on the end points of the integral itself (or, in thermodynamic terminology, the initial and final states of the system).
Important point: the internal energy depends only on the state of the system. So, by measuring the internal energy, we can tell how the system changed.

Analogy: path independence
- path independence of lifting an object 1 meter.
- the internal energy of a cup of tea just depends on it thermodynamic state – how much water and tea leaves it contains and what its temperature is. It does not depend on the history of how the tea was prepared (do you boil water in a kettle or in a microwave oven). The thermodynamics path that led to its current state is irrelevant as far as the change in internal energy because is path independent.

There are two special cases of the first law worth mentioning. A process that eventually returns a system to its initial state is called a cyclic process and another occurs in a free expansion where no work is done (W=0) and no heat is transferred (Q=0).

Cyclic Process
A process that eventually returns a system to its initial state (final state = initial state), the total internal energy change must be zero since it returns to its original state:

\[
\Delta E_{\text{int}} = \Delta E_{12} + \Delta E_{23} + \Delta E_{31} = 0 \quad \Rightarrow \quad E_{\text{int},f} = E_{\text{int},0} \quad \text{(cyclic process)}
\]

If a net quantity of work W is done by the system during this process, an equal amount of energy must have flowed into the system as heat Q. But there is no reason why either W or Q individually has to be zero.

Free Expansion
Think about the previous example we did when talking about heat transfer earlier. If W=0 and Q=0, the internal energy of an isolated system is constant:

\[
\Delta E_{\text{int}} = 0 = E_{\text{int},f} = E_{\text{int},0} \quad \text{(isolated system)}
\]

Problem-Solving Strategy
Set Up the problem using the following steps
- Units: \([W] = [Q] = [E_{\text{int}}] = \text{Joules} = J, [V] = \text{m}^3, [p] = \text{Pa}
  \quad [W] = [pV] = J
- The internal energy of the system is temperature dependent and only dependent on the internal (or microphysics) energies of the system. Higher \(K_{\text{micro}}\) & \(U_{\text{micro}}\), implies a higher internal energy whereas lower values lead to lower internal energy:
  \[
  \Delta E_{\text{int}} \propto T
  \]

1. Carefully define what the thermo system is and identify the initial and final states for each step.
2. Identify the known quantities and the target variables. Check whether you have enough equations. The first law can only be applied just once to each step in the process, so you will often need additional equations.
3. The work done occurs with there is a volume change. Unit wise, pressure is in Pa and volume is in m³ so that work is in joules. If heat capacity is given in terms of calories, convert it to joules.
4. The internal energy change \(\Delta E_{\text{int}}\) in any process or series of processes is independent of the path. Sometimes you will be given enough information about one path between the given initial and final states to calculate \(\Delta E_{\text{int}}\) for that path. Since \(\Delta E_{\text{int}}\) is the same or every possible path between the same two states, you can then relate the various energy quantities for other paths.
5. When a process consists of several distinct steps, it often helps to make a chart showing Q, W and \(\Delta E_{\text{int}}\) for each step. Then you can apply the first law to each line.
Example 18.1
A thermodynamic system is taken from an initial state A to another state B and back again to A, via state C, as shown by path ABCA in the pV-diagram.

a. (i) Complete the table filling in either ± for the sign of each thermodynamic quantity associated with each step of the cycle. (ii) Draw an energy bar diagram for each process.
b. Calculate the numerical value of the work done by the system for the complete cycle ABCA.

Solution

Process A → B:
Physically, in order to maintain a constant pressure as the gas is expanding, heat must be added and increase the collision rates in the system. That is, its temperature must increase (∆E_{int} > 0) as the system expands (W > 0). Although the work done BY the gas decreases it internal energy, the heat flowing in must be larger than the work: the first law states \( Q = W + ∆E_{int} \) must also be positive.

\[
\begin{align*}
Q_{AB} &> 0, \ W_{AB} > 0, \ ∆E_{AB} > 0
\end{align*}
\]

Process B → C:
In order to maintain a constant volume (W_{BC} = 0) and increase the pressure, one must increase the collision rate by heating the gas (Q_{BC} > 0). That is, there is a temperature increase and the internal energy increases: \( ∆E_{BC} = Q > 0 \).

\[
\begin{align*}
Q_{BC} &> 0, \ W_{BC} = 0, \ ∆E_{BC} > 0
\end{align*}
\]

Process C → A:
Since the process is cyclic, the starting and end points are the same. So the system returns to its original state and the change in internal is zero:

\[
\Delta E_{int} = \Delta E_{AB} + \Delta E_{BC} + \Delta E_{CA} = 0
\]

As we already discussed, we know that internal energies for processes AB and BC are positive. Therefore, the change in internal energy for \( \Delta E_{CA} \) must have decreased:

\[
\Delta E_{int} = 0 \quad \rightarrow \quad \Delta E_{CA} = -\Delta E_{AB} - \Delta E_{BC} < 0
\]

As the environment compresses (W_{CA} < 0) the piston, there are more collisions in the gas and this should increase the internal energy. (Note also that the magnitude of the work, |W_{CA}|, has the largest value of any of the works.) However, as just discussed, the internal energy decreases (\( \Delta E_{CA} < 0 \)), which implies the temperature decrease! The only way this can happen is if more heat is being transferred out of the system (Q_{CA} < 0) than work is being put in:

\[
Q_{CA} = W_{CA} + ∆E_{CA} < 0
\]

In other words, the magnitude of the work, |W_{CA}|, has the largest value of any of the works and therefore, the heat ejected must be even larger to reduce the internal energy. The energy bar diagram shows this clearly

\[
Q_{CA} < 0, \ W_{CA} < 0, \ ∆E_{CA} < 0
\]
b. The mathematically, the work is to sum up the areas under the curve:

\[ W_{\text{total}} = W_{AB} + \underbrace{W_{BC}}_{\text{constant volume}} + W_{CA} \]

\[ = \Delta p_{AB} \Delta V_{AB} + 0 + \left( \frac{1}{2} \Delta p_{CA} \Delta V_{CA} + \Delta p_{BA} \Delta V_{BA} \right) \]

\[ = \frac{20(3-1)}{40} + \left( \frac{1}{2} \left( 20 - 40 \right)(3-1) + 20(1-3) \right) = -20 \text{ J} = W_{\text{total}} \]

A more physical way is to calculate just the area of a triangle:

\[ |W_{\text{net}}| = \frac{1}{2} \Delta p \cdot \Delta V = \frac{1}{2} (2.0 \text{ m}^3)(20 \text{ Pa}) = 20 \text{ J} \]

Ranking the magnitudes of the works and the heats, we find that

\[ |W_{\text{CA}}| > |W_{\text{AB}}| > |W_{\text{BC}}| \quad \text{and} \quad |Q_{\text{CA}}| > |Q_{\text{AB}}| > |Q_{\text{BC}}| \]

Since process C \( \rightarrow \) A involves larger negative work (it occurs at higher average pressure) than the positive work done during process A \( \rightarrow \) B, then the net work done during the cycle must be negative.

\[ Q = W + \Delta E_{\text{int}} \quad \rightarrow \quad W_{\text{net}} = -20 \text{ J}; \quad Q_{\text{net}} = -20 \text{ J}; \quad \Delta E_{\text{int,net}} = 0 \]

**Example 18.2**

A sample of gas expands from 1.0 m\(^3\) to 4.0 m\(^3\) while its pressure decreases from 40 Pa to 10 Pa. Assume that \( E_{\text{int,1}} > E_{\text{int,2}} \). (a) (i) Rank the works, heats, and internal energies for processes A, B, and C, greatest first. (ii) Draw an energy bar diagram for each process. (b) (iii) How much work is done by the gas if its pressure changes with volume via path A, B, and C? Does this answer agree with part (a)? Assume that \( E_{\text{int,1}} > E_{\text{int,2}} \).

**Solution**

Physically, explain which path requires the most work done, the greatest heat flow, and the change in internal energy. Path A has the largest work since it has the largest area under the curve. Since the average pressure is the highest along path A it requires the largest heat in order to maintain it. On the other hand, path B has the second highest work done and heat flow since it has a higher average pressure than path C. Path C has the lowest W and Q. Since the internal energy is path independent, it will be the same for all 3 paths.

<table>
<thead>
<tr>
<th>Q</th>
<th>W</th>
<th>( \Delta E_{\text{int}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>32</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>42</td>
<td>–</td>
<td>+</td>
</tr>
</tbody>
</table>

a. Path A. The work along path A is
\[ W_A = W_{13} + W_{32} = \left( \text{area of rectangle} \right) + 0 \]

\[ = p_1 \Delta V = (40 \text{Pa})(4.0 \text{m}^3 - 1.0 \text{m}^3) = 120 \text{J} = W_A \]

b. Path B. The work along path B is

\[ W_B = W_{1-2} = \left( \text{area of triangle} \right) + \left( \text{area of rectangle} \right) \]

\[ = \frac{1}{2} (40 - 10)(4 - 1) + (10 - 0)(4 - 1) \text{ Pa} \cdot \text{m}^3 \]

\[ = \frac{1}{2} 45 + \frac{1}{2} 30 = 45 + 15 = 60 \text{J} = W_B \]

A more mathematical way is to integrate over path B, which requires that one finds the equation of the line: \( p = -10V + 50 \). Substituting this into the integral equation leads to

\[ W_B = \int_{1}^{4} p \text{ d}V = \int_{1}^{4} (50 - 10V) \text{d}V = (50V - 5V^2) \bigg|_{1}^{4} = 75 \text{J} = W_B \]

c. Path C. The work along path C is

\[ W_C = W_{14} + W_{42} = 0 + \left( \text{area of rectangle} \right) \]

\[ = p_2 \Delta V = (10 \text{Pa})(4.0 \text{m}^3 - 1.0 \text{m}^3) = 30 \text{J} = W_C \]

The most important analytical tool for thermodynamic processes is the 1st law. Now that we have the conceptual basis for it, we will move on now to calculate what goes on for various thermo processes:

1. Thermal Properties of matter; heat capacities and calorimetry
2. Heat transfer mechanism

**Temperature, Zeroth Law and Thermometers**

Now of course the concept of temperature seems such an intuitively obvious one that you might wonder why we need to discuss this at all (in fact, advance thermo courses usually spend a whole chapter just on temperature to discuss it). Temperature is simply a **measure of “hotness” or “coldness”**, so that we can say that a hot body has a higher temperature than a cold one. If two objects at different temperatures are placed in **thermal contact**, they are **able to exchange energy**. Since heat is the “thermal transition energy” to change states, “heat flows” spontaneously from the hotter to a colder body.

So, heat flows from the hotter to the colder body, we expect that the energy content and the temperatures of the two bodies will each change with time. After some time, the two objects have the same final temperature.

If any energy flows from the first to the second body, this is equal to the energy flowing from the second to the first body; thus, there is no net heat flow between the two bodies. The two bodies are said to be in **thermal equilibrium**, which is defined by saying that the energy content and the temperatures of the two bodies will no longer be changing with time and have the same temperature.
If various bodies are all in thermal equilibrium with each other, then we would expect that their temperatures should be the same. This idea is encapsulated in the zeroth law of thermodynamics:

**Zeroth law of thermodynamics**

Two systems, each separately in thermal equilibrium with a third, are in equilibrium with each other.

The zeroth law gives us some justification for how to actually measure temperature: we place the body whose temperature needs to be measured in thermal contact with a second body (thermometer), which displays some property that has a well-known dependence on temperature, and wait for them to come into thermal equilibrium. The zeroth law then guarantees that if we have calibrated this second body against any other standard thermometer, we should always get consistent results.

There are three different temperature scales: Celsius, Kelvin and Fahrenheit. To convert from one temperature scale to another,

\[
T_K = T_C + 273.15 \quad \Delta T_K = \Delta T_C \quad T_F = \frac{9}{5} T_C + 32
\]

### The Difference between Temperature, Heat, and Internal Energy

All matter is composed of continually moving atoms/molecules. Whether molecules combine to form solids, liquids, or gases depends on how fast the molecules are moving. That is, what determines the state or phase of a substance is related to the \( \Delta E_{\text{int}} \) of its atoms/molecules.

**Important Points**

1. The average KE of a system is directly related to the temperature. Whenever something becomes warmer, the KE of its particles has increased. For example, when one strikes a penny with a hammer, the mechanical work done by the hammer increases the internal energy of the penny and there are faster moving atoms.

\[
\text{Temperature } \propto K_{\text{avg}} \text{ of molecular motion}
\]

2. Temperature is NOT a measure of \( K_{\text{total}} \) (we now ignore PE since gas molecules are not bound) of the molecules in a substance. Think about this: there is twice as much molecular motion in a 2 liter than a 1 liter container of boiling water; however, the temperatures are the same since they have the same \( K_{\text{avg}} \).

3. If you touch a hot stove, energy enters your hand because the stove is warmer than your hand. When you touch a piece of ice, energy passes out of your hand and into the colder ice. **Heat Q** is the energy transferred from one thing to another because of a temperature difference.

**Key points:**

- **Heat is energy in transit from a higher temperature body to a lower temperature one.** Once transferred, the energy ceases to be heat.
Matter does not contain heat, it contains molecular KE

Units of Measurement: \( [Q] = \text{energy} = J \)

\[ 1 \text{ cal} = 4.1860 \text{ J} = 3.969 \times 10^{-3} \text{Btu} = \frac{1}{1000} \text{(Food cal)} \]

4. When heat is added, or removed from a substance, it affects the internal energy of the substance. The internal energy is the sum of all microscopic KE's (translation, rotational …) plus potentials:

\[
\Delta E_{\text{int}} = E_{\text{micro}} = K_{\text{translation}} + K_{\text{rotational}} + K_{\text{vibrational}} + \cdots + \text{all possible energies}
\]

Do single atoms have a temperature? What is meant by heat flow? Explain. Temperature is not a concept that has a lot of utility at the level of single atoms because it represents the mean kinetic energy of a group of particles (to within a coefficient). You can define it, it just doesn't help much. At the level of two atoms you revert to a more fundamental model such as the forces between them. One atom transfers energy to another through electromagnetic forces between them. When that energy manifests as randomized kinetic energy at the microscopic scale we refer to it as "heat" at the macroscopic scale.

For solids instead of gases, each of the atoms is jiggling around near a mean position defined by its relationship to the surrounding atoms (little imaginary springs). They are roughly harmonic oscillators, and they each have some energy. The temperature of each element is the mean energy of its atoms. But all the bits are connected, so over time the energy spreads out (each atom applies force to its neighbors as it jiggles; the ones that jiggle most apply the biggest forces...). On average, energy moves from regions of high mean energy to regions of low mean energy.

The temperature we are using is a low energy model

Explain the problem with temperature: Kelvin scale and (i) quantum and (ii) special relativity.

Thermal Properties of Matter and Calorimetry
When heat is added, or removed, a material’s internal energy changes. This change in internal energy manifests itself in two ways

Specific Heat Capacity and Temperature Change
When heating occurs such that a material changes temperature, it depends on (1) material, (2) temperature, and (3) mass.

1. Material Dependence
Have you ever noticed that some foods remain hotter much longer than others?
- The filling of hot apple pie can burn your tongue while the crust will not.
- A piece of toast can be eaten comfortably a few seconds after coming from a red-hot toaster. However, several minutes must be waited before one can enjoy hot soup.

Different materials have different capacities for storing internal energy. Unfortunately, this material characteristic (written in “old language”) is called the specific heat capacity (as if heat was contained in a material) for storing internal energy. Of course, heat is not in a material since it is energy is transit. Nonetheless, this is manifested in everyday language as being very hot/heat when we try to eat them.

**Question:** what do I mean by a really hot piece of pie when eating? There is a heat transfer via the pie to your cold mouth. Your low internal energy cold mouth (state-1)
experiences heating via the pie that results in a high internal energy hot mouth (state-2) (if you are not careful you end up with blisters):

2. Temperature Dependence
If you are heating water it requires 4200 J/kg to change the temperature by 1°C, whereas the same quantity of iron only requires 450 J/kg for the same temperature change. Different materials require different quantities of heating to change the temperature of a given mass of a material by a specified number of degrees.

3. Mass Dependence
A larger mass of water requires more time to reach its boiling point compare to a smaller mass of water. Different masses require different amounts of heating to raise the temperature.

In summary, water requires more heating ("absorbs more heat" – terrible language) than iron for the same temperature change. We say that water has a higher specific heat capacity than iron.

An example is those 4th of July-type sparkler: they emit sparks with a temperature of 2000°C but the heat one receives when one of these sparks land on one’s face or hands is very small. Sparks have small internal energy despite the fact of the 2000°C temperature.

Definition
The heating that occurs with there is a temperature change depends on the mass, material (specific heat), and the temperature change defined as

\[ Q = mc\Delta T \]

Units of measurement: \([c] = \frac{[Q]}{[m][T]} = \text{J/kg} \cdot \text{°C}\]

According to the specific heat capacity, it takes 1 cal (1 kcal or 4,186 J) to change the temperature of 1 gram (1 kg) of water by 1°C.

\[ c_{\text{water}} = 4,186 \text{ J/kg} \cdot \text{°C} = 1 \text{ cal/g} \cdot \text{°C} = 1 \text{ kcal/kg} \cdot \text{°C} \]

Definition
The specific heat capacity of any substance is defined as the quantity of heat required to change the temperature of a unit mass of a substance by 1°C.

Specific Heat Capacity \( c \)

Caution: The term specific heat does not use the word “heat” in the way that we have defined it. Specific heat is an old idea when heat was thought to be a substance contained in the object. The term has continued in use even though our understanding of heat has changed.

Inertia Analogy: Inertia is the resistance to changes in motion, the larger the mass, the greater the resistance to change in motion whereas the smaller the mass, the less resistance to changes in motion. The specific heat capacity acts like thermal inertia: the larger the specific heat, the greater the resistance to changes in temperature whereas the smaller the specific heat capacity, the less resistance to temperature change.

Interpretation
According to the specific heat, it takes 1 cal (1 kcal or 4,184 J) to change the temperature of 1 gram (1 kg) of water by 1°C.

\[ c_{\text{water}} = 1 \text{ cal/g} \cdot \text{°C} = 1 \text{ kcal/kg} \cdot \text{°C} = 4,184 \text{ J/kg} \cdot \text{°C} \]

If we rewrite the above heat equation,
\[
\frac{\Delta T}{Q} = \frac{1}{mc} \quad \text{steep slope} \quad \text{large heat capacity, small temp change } \Delta T
\]

\[
\frac{1}{mC} \quad \text{large heat capacity } C, \text{ small temp change } \Delta T
\]

Interpreting this equation implies it takes more energy to change the temperature of a substance with a large specific heat than to change the temperature of a substance with a small specific heat.

i. Metals, with small specific heats, has less ways to increase the KE of the iron molecules, so it warms up and cools down quickly. A piece of aluminum foil can be safely held within seconds of removing it from a hot oven.

ii. Water, with its very large specific heat, has more ways to increase the KE of the water (or storing internal energy) \(- K_t + K_{rot} + K_{vib}\), is slow to warm up and slow to cool down. This is fortunate for us. The large thermal inertia of water is essential for the biological processes of life. We wouldn’t be here studying physics if water had a small specific heat or life would be very different!

iii. Water has the highest heat capacity of all common natural materials. A relatively small amount of water absorbs a great deal of heat for a correspondingly small temperature change (it has a very large thermal inertia).

**Examples.** It is a very useful cooling agent and is used in cooling systems in engines. Antifreeze is NOT a natural material with its lime green or blue color and is manufactured! On the other hand, because of its large thermal inertia, it takes a long time to cool. Hot-water bottles used to be employed on cold winter nights before indoor heating and electric blankets where invented.

**Conceptual Question**

The desert sand is very hot in the day and very cool at night. What does this tell you about its specific heat? How about Space Shuttle tiles? How about the human body?

**Answer:** The sand has a low specific heat, as evidenced by its relatively large temperature changes for small changes in internal energy. As for the human body temperatures, the high value of \( c \approx c_{\text{water}} \) is one factor that helps us keep from rapid temperature changes.

**Space shuttle tiles** have a very low specific heat \( (c_{\text{tiles}} = 1256 \text{ J/kg·K}) \) because one does not want the shuttle tiles to absorb very much heat. If they had a large specific heat, they must absorb a lot of internal energy and eventually transfer this energy (as heat) to the inside of the shuttle. The space shuttle thermal protection system (TPS) is the barrier that protects the space shuttle during the searing 1650°C (3000° F) heat of atmospheric reentry. The glow is due to the tiles being heated until they are white hot (seen at the nose at upper right). A technician holding a tile seconds after being removed from a furnace at 1300°C. The tiles lose 90% of their heat within moments.

**Example 18.3**
A 50.0 g aluminum disk at 300°C is placed in 200 cm³ (or 0.158 kg) of ethyl alcohol at 10.0°C, then quickly removed. The aluminum temperature is found to have dropped to 120°C. The specifics are $c_{\text{Al}} = 900 \text{ J/kg} \cdot \text{K}$ and $c_{\text{ethyl}} = 2400 \text{ J/kg} \cdot \text{K}$.

a. (i) Physically explain the heat transfer between the aluminum disk and the alcohol and (ii) draw an energy bar diagram for the situation.

b. What is the new temperature of the ethyl alcohol?

**Solution**

Because there is a temperature change in the ethyl, the heat transferred between the disk and ethyl increases the $K_{\text{micro}}$ of the ethyl. (Why? Because there was a temperature change.) If we assume that the container holding the alcohol is well insulated, then the disk and ethyl interact with each other only. The first law states that the heat transferred from the disk changes the internal energy of the ethyl according to

$$\Delta E_{\text{int (ethyl)}} = Q_{\text{disk}} = mc_{\text{Al}}\Delta T \rightarrow \text{state-1(ethyl)} \quad \Delta E_{\text{int (ethyl)}} = mc_{\text{Al}}\Delta T \rightarrow \text{state-2(ethyl)}$$

The disk’s decrease in temperature is $\Delta T = 120°C - 300°C = -180°C = -180 \text{ K}$, and the heat transferred from the disk to the ethyl is

$$Q_{\text{Al}} = mc_{\text{Al}}\Delta T = 0.050 \text{ kg} \cdot 900 \text{ J/kg} \cdot \text{K} \cdot -180 \text{ K} = -8100 \text{ J}$$

$Q_{\text{Al}}$ is negative because the energy is transferred out of the aluminum. The ethyl alcohol gains 8100 J of energy so $-Q_{\text{Al}} = Q_{\text{ethyl}} = +8100 \text{ J}$. The change in the ethyl’s temperature is then

$$\Delta T = \frac{Q_{\text{ethyl}}}{mc_{\text{ethyl}}} = \frac{8100 \text{ J}}{0.158 \text{ kg} \cdot 2400 \text{ J/kg} \cdot \text{K}} = 21.4 \text{ K}$$

and its final temperature of the ethyl is

$$T_f = T_0 + \Delta T = 10°C + 21.4°C = 31.4°C = T_f$$

Typically, in conservation of energy problems we are not interested in the kinetic energy of the object but the velocity of the object. In thermal processes, we usually don’t go after the heat transferred but the temperature of the object.

The second type of heat transfer, when no temperature change occurs and results in a phase change of a material, we will now study.

**LATENT HEAT AND NO TEMPERATURE CHANGE**

Consider a glass of ice tea. If the temperature of the tea and ice are at equilibrium, then the temperature is 0°C. If the glass of ice tea is surrounded by room temperature, heat is transferred from the environment and into the glass, heating up the ice tea mixture. This process is evident since the ice melts after some time. However, the tea and ice mixture coexist and are still in thermal equilibrium at 0°C regardless of the fact that heat is entering the glass. NO temperature change occurs even though there is heat transferred!

**Question:** Where does all this heat transfer go to if it does not increase the temperature of the tea? Instead of increasing the $K_{\text{micro}}$, it goes directly into overcoming the intermolecular bonds given by $U_{\text{micro}}$ (which is effectively, the electrical potential energy of the system). **By overcoming the intermolecular bonds, the heat is causing a phase change from ice (solid) into water (liquid),** which we call melting the ice into water. Clearly, this is a different kind of heating since there is no temperature change.

**Definition**

The Latent Heat $L$ is the heat of transformation that must be added or removed in order to change the phase of a substance of a given mass: $Q = mL$.

Units of measurement: [L] = [Q]/[m] = J/kg

19.18
The possible types of phase transitions are

\[
\text{Solid} \xleftrightarrow{\text{add}} \text{Liquid} \quad \text{Latent Heat of Fusion} \equiv L_f
\]

\[
\text{Gas} \xleftrightarrow{\text{add}} \text{Liquid} \quad \text{Latent Heat of Vaporization} \equiv L_v
\]

\[
\text{Gas} \xleftrightarrow{\text{add}} \text{Solid} \quad \text{Latent Heat of Sublimation} \equiv L_S
\]

We will mostly be interested in two phase transitions:

**Interpretation of Phase Changes and Latent Heat**

Phase changes can be described in terms of a rearrangement of molecules when heat is added or removed from a substance.

1. **Latent Heat of Fusion \( \equiv L_f \) (transformations between a solids and liquids)**

   Latent Heat of Fusion is the heat of transformation either for a solid into a liquid or a liquid into a solid (e.g., either melt ice into water or freeze water into ice). A solid can be visualized using the spring model of an atom (atoms/molecules are bound by "electrical springs," which represent the binding energy of the attractive electric force. When heating a solid, the atoms/molecules begin to oscillate with a vibration amplitude and increases in size until they have enough energy to overcome the binding energy of the atoms. This is called the melting point of the solid. The **HEAT OF FUSION** is the amount of **energy that must be removed to fuse the liquid molecules into a solid and vice versa.** In other words, phase transition to a solid, the \( K_{\text{avg}} \) of the liquid molecules must be reduced so that the electrical attractive force is enough to bind molecules into a crystalline structure.

2. **Latent Heat of Vaporization \( \equiv L_v \) (transformations between a gases and liquids)**

   Latent Heat of Vaporization is the heat of transformation either for (i) liquid into a gas or (ii) a gas into a liquid (e.g., boil water into water vapor or condense water vapor into liquid water). In a very similar manner, the molecules in a liquid have stronger binding energies compared to those in a gas. When going from a liquid state to a gas state, heating the liquid will increase the \( K_{\text{avg}} \) of the molecules such that they overcome the electrical binding energy to "vaporize" these bonds. Once this is completed, one has phase transitioned from a liquid to a gas. The **HEAT OF VAPORIZATION** is the amount of **energy that must be added to a liquid to change into a gas.** Of course, to phase transition from a gas to a liquid, heat must be remove to reduce the \( K_{\text{avg}} \) such that the electrical binding energy can do it job and form more bonds. Again, this amount of energy **removed** is called the **heat of vaporization.**

3. **Latent Heat of Sublimation \( \equiv L_S \).** Example: dry ice vaporizing into a \( \text{CO}_2 \) gas or remove heat from the air in your freeze forms frost (cooling coils). Other examples (moth balls, Dye sublimation color printer, Sublimation of water from frozen food causes freezer burn).

4. **Superfluids, superconductivity, …**

5. The work/heat used to overcome the binding energy depends on the force and the distance the atoms are removed. Since the average distance between atoms in gases are much farther than in either the liquid or the solid phase, we expect more work/heat required to vaporize a given mass than to melt it. As a result, the **heat of vaporization is much larger than the heat of fusion: \( L_v > L_f \).**

<table>
<thead>
<tr>
<th>Substance</th>
<th>( T_{\text{melting}}(\degree\text{C}) )</th>
<th>( L_f(10^5 \text{ J/kg}) )</th>
<th>( T_{\text{boiling}}(\degree\text{C}) )</th>
<th>( L_v(10^5 \text{ J/kg}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>-210</td>
<td>0.26</td>
<td>-196</td>
<td>1.99</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>-114</td>
<td>1.09</td>
<td>78</td>
<td>8.79</td>
</tr>
<tr>
<td>Mercury</td>
<td>-39</td>
<td>0.11</td>
<td>357</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>3.33</td>
<td>100</td>
<td>22.6</td>
</tr>
<tr>
<td>-------</td>
<td>-----</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>328</td>
<td>0.025</td>
<td>1750</td>
<td>8.58</td>
</tr>
</tbody>
</table>

The important latent heat values:

\[
L_f(\text{water}) = 3.35 \times 10^5 \text{ J/kg} \\
L_v(\text{water}) = 2.26 \times 10^6 \text{ J/kg}
\]

**Example**

Consider the heat required to convert a 1-g block of ice at –25°C to steam at 125°C. The material dependent constant that is associated with changing the temperature of a material, is the specific heat. The specific heats for ice, water and steam are

\[
c_{\text{ice}} = 2.09 \times 10^3 \text{ J/kg°C}, \\
c_{\text{water}} = 4.19 \times 10^3 \text{ J/kg°C}, \\
c_{\text{steam}} = 2.01 \times 10^3 \text{ J/kg°C}.
\]

**Part A:** Since the ice is below 0°C, we first have to warm-up the ice to 0°C to start the melting process. Therefore, to change the temperature of the ice from –25°C to 0°C, the amount of heating is connected with the specific heat:

\[
Q_A = m_{\text{ice}}c_{\text{ice}}\Delta T = (10^{-3} \text{ kg})(2090 \text{ J/kg°C})(25°C) = 52.3 \text{ J}
\]

Physically, this amount of heating goes into increasing the motion of the bound molecules without starting to break the molecular bonds.

**Part B:** When ice reaches 0°C, the ice/water mixture will remain at 0°C even though heating continues. This heating does not increase the overall average KE of the water molecules but goes into breaking the molecular bonds first. It is this process that phase transitions the ice to water. Once these bonds are broken, then a temperature change can occur. The heating required to phase transition the 1-g of ice into 1-g of water is the latent heat of fusion:

\[
Q_{\text{fusion}} = Q_B = mL_f = (10^{-3} \text{ kg})(3.33 \times 10^5 \text{ J/kg}) = 333 \text{ J}
\]

**Part C:** With all of the bonds broken, now heating can change the average KE of the molecules and increase it such that there will be a measurable change in temperature. Heating that results in changing the temperature (or internal energy) of the water from 0°C to 100°C is

\[
Q_C = m_wc_w\Delta T = (10^{-3} \text{ kg})(4.19 \times 10^3 \text{ J/kg°C})(100°C) = 4.2 \times 10^5 \text{ J}
\]

Note that this quantity \(Q_C\) is larger than \(Q_B\) – why? There is more heating since the water molecules are being separated by a farther distance. In the language of Phys 4A, it requires more “work” to move objects farther apart. Heating and work are interchangeable in this setting.

**Part D:** As liquid water reaches 100°C, we are all familiar with the fact that water is boiling to become steam. In other words, liquid water is phase transitioning to water
vapor. change occurs as the water changes from water to 100°C to steam at 100°C. The heating required to phase transition the 1-g of water into 1-g of steam is the latent heat of vaporization:

\[ Q_{\text{vaporization}} = Q_D = mL_v = (10^{-3}\text{ kg})(2.26 \times 10^6 \text{ J/kg}) = 2.3 \times 10^3 \text{ J} \]

Note that this quantity \( Q_D \) is larger than \( Q_B \) – why? Once again, it requires more heating to separate the vapor molecules farther apart and therefore, \( L_{\text{vaporization}} \gg L_{\text{fusion}} \).

**Part E:** With all of the liquid bonds broken, now heating can change the average KE of the vapor molecules and increase its temperature average KE (or average KE). Heat is being added to the steam with no phase change occurring. Heating that results in changing the temperature (or internal energy) of the water vapor from 100°C to 120°C is

\[ Q_e = m_c c_v \Delta T = (10^{-3}\text{ kg})(2.01 \times 10^3 \text{ J/kg°C})(25°C) = 50.3 \text{ J} \]

Note that this quantity \( Q_e \) is quite small and is comparable to \( Q_A \) – why? In both cases the extra effort in separating the vapor molecules and ice molecules results in very little distance change. Consequently, this implies that very little heating is required to only move these molecules far enough to setup phase transition states.

**Summary**

Drawing out an energy bar diagram (assuming no work is done) leads to

Comparing the heat energies relative to each other and to the total heat added, we find

\[ Q_{\text{vaporization}} > Q_{0 \text{ to } 100°C} > Q_{\text{fusion}} > Q_{-25 \text{ to } 0°C} > Q_{100 \text{ to } 125°C} \]

\[ Q_{\text{vaporization}} / Q_{\text{total}} = 73.7\% \]
\[ Q_{-25 \text{ to } 0°C} / Q_{\text{total}} = 1.6\% \]
\[ Q_{100 \text{ to } 125°C} / Q_{\text{total}} = 1.7\% \]

**Physical interpretation**

Note two things: (i) \( Q_{-25 \text{ to } 0°C} \approx Q_{100 \text{ to } 125°C} \) are approximately equivalent and very small and (ii) \( Q_{\text{vaporization}} \) is much larger than all of the other heats combined. **What physical reason explain these values?** When heating up the ice, the separation of the ice molecules at –25°C is roughly the same when ice is at 0°C. So the heating required is very small. Similarly, the same can be said about heating steam from 100°C to 120°C, the separation of vapor molecules is roughly about the same. On the other hand, \( Q_{\text{vaporization}} \) is much larger than all of the other transitional heatings because vaporization requires more heat to separation the molecules farther apart.

**Calorimetry**

Continuing the same type of thinking, we will continue focusing on how heating is transferred between a hotter object and a cooler object. An process of measurement of this heating is called a *calorimeter* and we assume that the only way to change the internal energy of the system is through heating only \( Q - 0 = Q = \Delta E_{\text{int}} \). That is, the
heating entails the hotter object transferring its heat energy to the cooler object until the system is allowed to reach thermal equilibrium.

**DEMO** Calorimetric setup plus a metal block

**Example: A hot block is dropped into a container of cooler water.**

The heat from the hot block changes the internal energy of the water and the container (assume none escapes into the environment). Physically, in the language of the first law, the hotter object changes the internal energy of the water plus the container. On the other hand, the “energy lost” by the hotter object must be the “energy gained” by the cooler water and container:

\[
-Q_{\text{hotter object}} = \Delta E_{\text{int}} = (Q_{\text{cooler water}} + Q_{\text{container}})
\]

\[
\text{(heat transfer by the hot object)} = \text{(changes the internal energy of the cold water & container)} = \text{(heat gained by the water & container)}
\]

\[
-Q_{\text{lost (block)}} = \Delta E_{\text{int}} = +Q_{\text{gain (water + container)}}
\]

So what I did was follow the energy flow via the first law.

**Problem-Solving Strategy for Calorimetry**

Identify the relevant concepts: (i) if there is a temperature change then one must use the specific capacity type heating that calculates the amount of increase or decrease in the \(K_{\text{micro}}\) of the system. (ii) if there is no temperature change then one must use the latent heat type heating that calculates the amount of increase or decrease in the \(U_{\text{micro}}\) of the system. So the first law state that the amount of heat lost by one body must equal the amount gained by the other body.

\[
-Q_{\text{lost}} = \Delta E_{\text{int}} = +Q_{\text{gain}}
\]

Step 1: Identify which objects are either “loosing” or “gaining” internal energy. To avoid confusion with algebraic signs, any object loosing internal energy (or “loosing” heat) will have a negative sign while any object gaining internal energy (or “gaining” heat) is positive.

Step 2: Each object will either undergo one or both of the following:

- temperature change
  - with no phase change: \(Q = mc\Delta T\)
  - phase change with no temperature change: \(Q = mL\)

Step 3: Consult a table for values of the specific heat (or molar heat capacities), latent heats of fusion and vaporization.

**Example 18.4**

Two 50 g ice cubes are dropped into 200 g of water in a thermally insulated container. The water is initially at 25°C and the ice comes directly from a freezer at −15°C.

a. (i) Physically explain if only part of the ice melts or all of the ice melts? (ii) Now draw a (ii) \(T\) vs. \(Q\) diagram and an (iii) energy bar diagram for the situation.

b. What is the final temperature of the water? If only part of the ice melts, how much of it is left?

**Solution**

a. There are two possibilities: (i) all of the ice melts or (ii) part of the ice melts. That is,

- The system reaches thermal equilibrium at the melting point of ice, with some of the ice melted.
- All of the ice melts and the system reaches thermal equilibrium at a temperature at or above the melting point of ice.
Picturewise, what is the difference between these two situations?

OR

Is the amount of energy in the water enough to melt all of the ice?

To determine which scenario we have, calculate how much heating is transferred from the water to the ice when the water reaches 0°C as well as how much energy is required to melt all of the ice.

The amount of “heat lost” of the water to reach 0°C is

\[
-Q_{\text{water}} = -c_{\text{water}} m_{\text{water}} (T_f - T_{\text{water},0})
\]

\(\text{take water from 25°C to 0°C}\)

\(c_{\text{water}} = 4190 \text{ J/kg K} \quad m_{\text{water}} = 0.200 \text{ kg} \quad T_{\text{water},0} = 25°C\)

\[-(4190 \text{ J/kg K})(0.200 \text{ kg})(0°C - 25°C) = 2.10 \times 10^4 \text{ J} = 210 \text{ kJ}\]

Is this amount of energy enough to melt all of the ice?

- The system reaches thermal equilibrium at the melting point of ice, with some of the ice melted.
- All of the ice melts and the system reaches thermal equilibrium at a temperature at or above the melting point of ice.

How much heat is required to melt all of the ice?

\[
Q_{\text{melt ice}} = c_{\text{ice}} m_{\text{ice}} (T_f - T_{\text{ice},0}) + m_{\text{ice}} L_f (\text{water})
\]

\(\text{take ice from -15°C to 0°C}\)

\(c_{\text{ice}} = 333 \times 10^3 \text{ J/kg K} \quad m_{\text{ice}} = 0.100 \text{ kg} \quad T_{\text{ice},0} = -15°C\)

\(L_f = 333 \times 10^3 \text{ J/kg} \quad m_{\text{water}} = 0.200 \text{ kg} \quad T_{\text{water},0} = 25°C\)

\[= \left(0.33 \times 10^5 \text{ J} \right)(0.100 \text{ kg})(0°C - (-15°C)) + \left(3.33 \times 10^4 \text{ J/kg} \right)(0.100 \text{ kg})(333 \times 10^3 \text{ J/kg})\]

\[= 3.66 \times 10^4 \text{ J}\]

The amount of heat in the water above 0°C is

\[|Q_{\text{water}}| = c_{\text{water}} m_{\text{water}} (T_f - T_{\text{water},0})\]

\(\text{take water from 25°C to 0°C}\)

\(c_{\text{water}} = 4190 \text{ J/kg K} \quad m_{\text{water}} = 0.200 \text{ kg} \quad T_{\text{water},0} = 25°C\)

\[= (4190 \text{ J/kg K})(0.200 \text{ kg})(0°C - 25°C) = 2.10 \times 10^4 \text{ J}\]

Since \(Q_{\text{melt ice}} > |Q_{\text{water}}|\), not all the ice melts and therefore, some ice remains. Plotting a \(T\) vs. \(Q_{\text{added}}\) curve yields the picture.
b. The equilibrium temperature is clearly 0°C! The next question is how much ice mass remains? There are two ways to approach this: (i) physics or (ii) mathematical approach. From the physics viewpoint, the bar diagram shows us that

**Physics Approach**

From the physics viewpoint, the bar diagram shows us that the energy available to melt the ice must be

\[
Q_{\text{water}} = Q_{\text{warm-up ice}} + Q_{\text{available}} = Q_{\text{water}} - Q_{\text{warm-up ice}}
\]

\[
= 20,950 \text{ J} - 3330 \text{ J} = 17,620 \text{ J}
\]

That is, 17,620 J goes into melting ice. Therefore, the amount of melted ice is

\[
Q_{\text{available}} = 17,620 \text{ J} = m_{\text{melted ice}} L_f (\text{water})
\]

\[
m_{\text{melted ice}} = \frac{Q_{\text{available}}}{L_f (\text{water})} = \frac{17.6 \times 10^3 \text{ J}}{333 \times 10^3 \text{ J/kg}} = 0.0529 \text{ kg}
\]

The amount of ice left in the container is

\[
m_{\text{unmelted ice}} = m_{\text{total}} - m_{\text{melted ice}} = (0.100 - 0.0529) \text{ kg} = 0.0471 \text{ kg} = 47.1 \text{ g}
\]

**Mathematical Approach**

From the first law, the heat lost from the water must increase the internal energy (temperature) of the ice. As we already concluded, the final temperature of the ice-water mixture is \(T_f = 0\text{°C}\) and so the first law states

\[
-Q_{\text{lost by water}} = \Delta E_{\text{int (ice)}} = +Q_{\text{gained by ice}}
\]

\[
-c_w \frac{m_w}{m_w} (T_f - T_{w0}) = c_{icw} m_{icw} (T_f - T_{icw,0}) + m_{\text{melted ice}} L_f (\text{water})
\]

Solving for the mass of the melted ice,

\[
m_{\text{melted ice}} = \frac{c_w m_w T_{w0} + c_{icw} m_{icw} T_{icw,0}}{L_f}
\]

\[
= \frac{(4190 \text{ J/kg°C})(0.200 \text{ kg})(25°C) + (2220 \text{ J/kg°C})(0.100 \text{ kg})(-15°C)}{333 \times 10^3 \text{ J/kg}}
\]

\[
= 5.29 \times 10^{-2} \text{ kg} = 52.9 \text{ g} = m_{\text{melted ice}}
\]

This is the same answer as above and immediately leads to 47 g of remaining ice.

**Conceptual Question**

In some household air conditioners used in dry climates, air is cooled by blowing it through a water-soaked filter, evaporating some of the water. How does this cool the air? Would such a system work well in a high-humidity climate? Why or why not?

**Answer:** When the water changes phase from liquid to vapor, heat energy must flow into it. The heat energy comes out of the air so the air is cooled. The water evaporates more
readily if the humidity is high, so such a system works less well in a high-humidity climate.

Desert travelers sometimes keep water in a canvas bag. Some water seeps through the bag and evaporates. How does this cool the water inside?

**Answer:** Heat energy flows into the water as it undergoes the phase change associated with evaporation. This heat comes from the water inside the bag and when heat leaves this water, its temperature decreases. A similar thing happens when your first step out of the shower: you feel cold but as soon as you dry you feel warmer, even though the room temperature has not changed. Why? That's because as water evaporates from your skin, it removes the heat of vaporization from their bodies. To stay warm, immediately dry off so no heat is lost.