Thermodynamics

What you'll learn:

- What is conservation of mass?
- What is conservation of energy?
- Types of energy
- What is work?
- Is water really always a solid at 0°C?

Motivation

Most people know that you can never get something for nothing. You can’t get an ice cream cone from the ice cream man without paying for it, and you can’t get your air conditioner to work without giving it some electricity. When you give the air conditioning electricity, however, is your air conditioner actually working? The true answer is no. In order to do work the air conditioner would have to be using the energy supplied to move something. Instead it is converting the electric energy supplied to a different kind of energy that does not take part in work. So when you say “my air conditioner isn’t working”, you don’t know how right you are!

Thermodynamics and types of energy

We can define thermodynamics as the study of energy in a system. In order to study energy, we will define several types. Internal energies are the energies associated with the molecules and atomic structures of a system. Mechanical energies are the energies associated with the ability to do work.

Mechanical energies include:

**Kinetic energy: (KE):** energy due to motion of the system

**Potential energy: (PE):** energy due to elevation in a gravitational field. Some physics books define this as readily available energy for work.

Internal energies are usually denoted as a single value (U), where \( U = \sum \text{internal energies} \). They include:
**Sensible energy**: energy due to the motion of the molecules

**Latent energy**: energy associated with the phase of a system.

**Chemical energy**: energy associated with atomic bonds.

**Nuclear energy**: energy associated with the strong bonds in the nucleolus of the atom.

The total energy is the sum of all the energies discussed above:

\[ E = KE + PE + U + E_{\text{other}} \]

\( E_{\text{other}} \) can be an electrical energy (energy associated with electrons moving), a heat energy (energy associated with temperature difference), or some other external energy acting on the system.

It is often convenient to talk about specific values. Specific values are values per unit mass. For example specific Volume = volume/mass = 1/density = 1/ρ = \( v' \). For all values, we use a small case letter for specific values except for the specific volume where we use \( v' \) so as not to confuse it with velocity. For example specific kinetic energy is \( ke = KE/m \).

\[ e = ke + pe + u + E_{\text{other}} \]

Now, it is important to understand how to obtain the different mechanical energies:

\[ KE = \frac{1}{2} mv^2 \]

\[ PE = mgz \]

Where \( m \) is mass, \( v \) is the system velocity, \( g \) is acceleration due to gravity, and \( z \) is elevation above a reference point.

If a ball is thrown up into the air its kinetic energy starts high and its potential energy starts low. As the ball gets higher it slows down and its \( ke \) is decreased. What happened to the \( ke \)? It has not been destroyed; instead it was transferred to \( pe \). This is clearly stated in the **Conservation of energy principle**. Conservation of energy states that energy cannot be created or destroyed. It can only be transferred to another form! In other words:

Energy going into a system – Energy going out of a system = Energy change in the system.

**Some laws of thermodynamics**

This is the **first law of thermodynamics**. If you have a system that says to supply it with 30kJ of energy and you know you will only get 15kJ of energy out the other 15kJ of energy is not destroyed! It is lost to things like waste heat from the friction of moving parts. In fact, heat is a very common
form of energy transfer! In fact, E\text{other} is very often heat (Q). Heat is defined, again, as the energy that is transferred by a temperature difference.

**Example:**

![Figure 1](image)

**There is no heat transfer of energy between the cup and the room because there is no temperature gradient.**

Heat naturally moves from hot to cold. Cold is an absence of heat. Therefore when you pick up a cold soda you cannot correctly say that you feel the cold going into your hand! What you feel is the heat leaving your hand. When the heat leaves to go to the cold temperature there is a temperature change that is felt. This brings us to the **Zeroth law of thermodynamics**: if system A is thermal equilibrium with system B, and system C is in thermal equilibrium with system B, then system A is in thermal equilibrium with system C. Equilibrium can be defined as the state that exists after a system stops changing (i.e. no amount of time passing will change the system). Equilibrium is identified if, when you change a system slightly, it tends to go back to that equilibrium state. For example if you have room temperature water sitting in a cup and you want to know if that is equilibrium you may heat the cup so the water temperature increases. Then you wait and find that the cup once again returns to the room temperature state. You see that after it turns to room temperature no other changes are seen in the temperature. This is an equilibrium state for the glass of water.
Example:

The heat moves from the 50K section cooling it. It moves into the 20K section heating it.

If you can’t create or destroy energy what happens in real machines since we always get less energy out then we put in? The answer is losses. Areas of loss include heat exchange, friction; energy is used to work other parts, chemical reactions, etc. How good a system outputs can be shown with efficiency. **Efficiency** ($\eta$) is a measure of how good a system translates input energy to useful energy.

$$\eta = \frac{\text{Energy output}}{\text{Energy input}} = \frac{\text{Power output}}{\text{Power input}}$$

**Example:**

If I supply a turbine with 60J of electrical energy and the turbine can do 30J of work what is the efficiency of the turbine?

$$30J/60J = .5$$

50% efficient

**Example:**

You input 100J of energy into a fan that is 20% efficient. The fan works to power a heater that is only 10% efficient. A) How much energy does the heater put out? B) What are the total losses in the system?
A) \[ \eta_{\text{fan}} = 0.2 = \frac{E_{\text{out of fan}}}{E_{\text{into fan}}} = \frac{E_{\text{out of fan}}}{100} \]

\[ E_{\text{out of fan}} = 20 \text{J} \]

\[ \eta_{\text{heater}} = 0.1 = \frac{E_{\text{out of heater}}}{E_{\text{out of fan}}} = \frac{E_{\text{out of heater}}}{20} \]

\[ E_{\text{out of heater}} = 2 \text{J} \]

B) \[ E_{\text{in}} - E_{\text{out}} = E_{\text{loss}} \]

\[ 100 - 2 = 98 \text{J} \]

If you hold a 1000K rod to a board of wood for one ten seconds the wood will only change temperature a little. If you hold the same rod up to a board made of aluminum for ten seconds, the aluminum temperature will change greatly even if it started at the same temperature as the wood. It is convenient to have a quantity that is used to help express how much heat is needed to change the temperature of a substance. The specific heat \((c)\) of a substance is the energy required to raise one unit of mass of a substance by one degree Celsius. There are two types of commonly used specific heat values. One is the specific heat of a substance at a constant pressure \(c_p\) and the other is the specific heat when the substance is at a constant volume \(c_v\). If a gas were in a cylinder that was closed whose size was unchanging, one would use \(c_v\) to determine heat and temperature changes. If a gas was in a piston cylinder device one would use \(c_p\).
Here, \( u \) is the specific internal energy, \( T \) is the temperature in kelvin, \( V \) is the volume, \( h \) is the enthalpy (a quantity that includes \( u \) and \( T \). \( h = u + RT \), where \( R = 8.314 \text{ kJ/(kmol K)} \)), and \( P \) is the pressure. \( c_p \) and \( c_v \) are often constant quantities in pure substances.

**Example:**

If a small hot rod \( T=2000\text{K} \) is in a large room at \( T=300\text{K} \), as time goes to infinity what will the temperature of the rod and room be?

They will both be at room temperature. If the room is large enough the heat transfer from the hot rod may not be enough energy to raise the temperature of all the air in the room.
Phases of matter

A pure substance is a substance whose chemical composition is fixed. This means that if you were to take a chunk of the substance in one spot and another chunk from another spot, the chunks composition would be identical.

Example: Is this a pure substance?

<table>
<thead>
<tr>
<th>Substance</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous air</td>
<td>Yes</td>
</tr>
<tr>
<td>Any single elemental compound (N₂, O₂...)</td>
<td>Yes</td>
</tr>
<tr>
<td>Sugar mixed in water</td>
<td>No... there may be more sugar in one part then another.</td>
</tr>
<tr>
<td>Mix of liquid and gaseous water</td>
<td>Yes even though there are two substances, the overall composition is consistant</td>
</tr>
</tbody>
</table>

Any pure substance can be described as being in one of several phases. A phase is the state of which the substance is in. Phases include:

Solid: In a solid molecules are packed tightly together and form a repeating lattice pattern. The molecules stay fixed together in their positions because of the strong force between molecules. This is why solids keep their shape, even under moderate force.

Example: If you stand on a rock it does not change shape. The strong bonds of the molecules are strong enough to resist the force of your weight.

Liquid: In a liquid the molecules are spaced close together, but do not have the strong atomic bonds like in a solid. Therefore the molecules positions are not fixed and the substance deforms easily.

Example: Milk takes the shape of both the carton and the glass. The force of gravity is enough to push the milk to the sides of any container. Much more on liquids will be discussed in the fluids lessons in this class.

Gas: In a gas molecules are far apart and free to move about. There is no sort of molecular order so a gas will fill any container. Therefore a gas volume = container volume.
Example: If you heat a balloon it expands. The same amount of air molecules fill the bigger balloon as well as they did the smaller cool balloon.

Plasmas are another phase, but will not be covered in this class.

Substances can transition between phases because of a temperature change. Any child will tell you that water freezes at 0°C and boils at 100°C. Graphically, for many substances:

![Figure 5](image)

It is important to notice that at the transitions between phases the temperature does NOT change! For water at 0°C, both solid and liquid can be present! The temperature does not change during phase change because all of the energy is going into the phase change which leaves none for temperature change.

Did you know high up in the mountains, where the air is thinner, it is easier to boil water? Pressure effects how phases change with temperature. For water the graph we just drew (only looking at the liquid/gas sections) would change at different pressures as follows:

![Figure 6](image)
You can see that at a low enough pressure, you can get boiling at a lower temperature than expected. Also, at high enough temperature liquid water can exist well over 100°C. The temperature at which the transition occurs between liquid and gas is called the **saturation temperature**. For a given fluid and a given pressure, this can be looked up.

Flipping the variables, let’s hold the temperature constant and change the pressure of the same substance.

We noticed from the figure 6 that as we lower the pressure, a lesser amount of temperature is needed for phase change. Here we notice the same thing; at a lower temperature transition occurs at a lower pressure. The pressure for which the transition to gas occurs at a given temperature is called the **saturation pressure**. This pressure may be looked up if the temperature and substance is known.

**Example:**

A pure substance is in liquid form in a piston cylinder device. The substance is heated until the saturation temperature is reached. Suddenly a weight is added to the piston making it heavier, but keeping the temperature the same. The temperature continues to rise until the entire substance is in the gas phase. Draw the process that the system underwent on a T-V diagram.
What happened here? The volume increases with temperature as $T$ goes to $T_{\text{sat}}$. It stays along a constant pressure line because the pressure in a typical piston cylinder device is constant and dependant on piston weight. When the pressure is increased a new constant pressure line is followed with the increase in temperature until a new $T_{\text{sat}}$ value is reached. As phase change occurs, the volume changes because the liquid is transforming into gas (the molecules are farther apart in a gas so the volume increases with more gas). The temperature begins to increase again when all of the substance is gaseous.

**The Ideal Gas**

These graphs lead us to believe that there should be a relation between $P$, $V$, and $T$. In fact any equation that relates pressure, specific volume, and temperature is called an **equation of state**. The most famous equation of state is probably the ideal gas law. It states that:

$$PV = nR_u T, \quad PV = mRT, \quad P = \rho RT$$

Where $P$ is the pressure, $V$ is the volume, $R_u$ is the ideal gas constant and is equal to $8.314 \text{kJ/Kmol*K}$, $R = R_u/\text{molar mass}$, $n$ is the number of moles in a substance, $m$ is the mass of the gas, and $\rho$ is the density (which is $1/\text{specific volume}$). $R$ is a constant for any given gas and can easily be looked up in a table of gas constant values.

When can we assume a gas is ideal?

1. When the pressure is very low, but the entire pure substance is gaseous.
2. At very high temperatures
3. If the gas has a very low density
The more of these three criterions that are met the more ideal a gas is.

“Good” ideal gasses include air, nitrogen, hydrogen, oxygen, helium, argon, neon, and krypton.

Example: One mol of helium is in a piston cylinder device. The piston weighs 20N, has an area of 1m², and is free to move. There is a vacuum above the piston so no atmospheric pressure is felt on the piston or the gas. The gas in the cylinder is heated 100K above what it was originally. Assuming helium is an ideal gas, what is the change density in state 2 with respect to the density in state 1? For helium \( R = 2.08 \times 10^3 \text{ J/kg*K} \).
\[ \frac{P_1}{\rho_1 T_1} = R = \frac{P_2}{\rho_2 T_2} \]
\[ \frac{1}{\rho_1} * \frac{1}{T_1} = \frac{1}{\rho_2} * \frac{1}{T_1 + 100} \]

and

\[ P_1 = \rho_1 R T_1 \]
\[ \frac{20 Pa}{(2.08 \times 10^3 J/kg*K)} \left( \frac{1}{\rho_1} \right) = T_1 \]

\[ \frac{1}{\rho_1} * .0096 = T_1 \]

\[ \frac{1}{\rho_1} * .0096 = \frac{1}{\rho_2} * \left( \frac{1}{.0096 * \frac{1}{\rho_1}} + 100 \right) \]

\[ 104 = \frac{1}{(.0096 * \frac{\rho_2}{\rho_1}) + (\rho_2 * 100)} \]

\[ 104 * \left[ (.0096 * \frac{\rho_2}{\rho_1}) + (\rho_2 * 100) \right] = 1 \]

\[ \frac{\rho_2}{\rho_1} + \rho_2 * 10400 = 1 \]

\[ \rho_2 = \frac{1}{\frac{1}{\rho_1} + 10400} \]

The ideal gas law is not the only equation of state, but it is the easiest to use and is sufficient in a large number of applications.
We know that energy can’t be created or destroyed, but when we add heat to a piston cylinder device where does the energy go? The answer is work. **Work** is an energy transfer that moves and object. If nothing is moved, there was no work done. For instance, if you push on a wall for hours will all your might the wall will probably not budge. You may get tired and say you did a lot of work, but really you have done no work at all! This becomes clearer when we define work (W) with the equation:

\[ W = F \Delta x \]

Or work is equal to a force on an object; multiplied by the distance the object was moved. Expanding upon this equation:

\[ F = PA \]

\[ W = PA \Delta x \]

\[ \Delta x = \Delta V \]

\[ W = P \Delta V \]

Or, if we look at infinitesimal volume changes:

\[ W = \int P \, dV \]

Recall the P-V diagrams we discussed earlier in this section. Let’s just consider the fully gaseous portion of the graph:

*Figure 10*

Example: A piston cylinder device is at steady state. Heat is added increasing the temperature. Suddenly the piston has weight taken from it quickly enough that the volume of the gas in the cylinder is unchanged. Then an equal amount if heat that was added in step one is now taken away. Finally the weight that was taken off of the piston is put back on. Draw the P-V diagram and shade the section that represents the work done on the boundaries (i.e. the work done to move the piston throughout the cycle).
A: At first the pressure is constant but the volume increases with increasing temperature (volume increases with heat added)

B: When the weight is taken from the piston the pressure becomes less

C: As heat is taken from the piston (at this new constant pressure) the volume decreases

D: When the weight is put back on the pressure increases in the system.

The work area is shaded. In part A the work (designated by all the area under line A) is positive (as the piston moves up V(final) > V(initial)), but in part c the work (designated by the area under line c) is negative (because V(final) < V(initial)). In parts B and D there is no work because there is no change in volume. The total work is the sum of the work done by all parts. Area under A – Area under C + 0 + 0 = area shaded in figure 11.

Recall: The conservation of energy principle stated that energy could not be created or destroyed. There is also a conservation of mass principle. Conservation of mass in its most basic statement says that mass cannot be created or destroyed. Later in this class when we go into fluids we will expand upon this, but for now it is sufficient to understand the mass into a system minus the mass out is equal to the change of mass in the system. In many cases the change of mass is mass storage. In other words:

\[ m_{\text{in}} - m_{\text{out}} = m_{\text{change}} \]

{As an interesting side note: In case you are thinking that new particle physics makes the conservation of mass incorrect, recall that energy is related to mass (when objects are moving close to or above the speed of light, \( E = mc^2 \) + function of mass and velocity), so we will have no discussion of whether the new LHC (large hadron collider) will “create” mass from nothing! It too follows the conservation of mass, it just combines the principle with the conservation of energy.}
A **mass flow rate** is defined as the amount of mass that flows across an area per unit time.

\[
\dot{m} = \frac{\partial m}{\partial t} = \rho A \cdot v
\]

where \( m \) is the mass, \( t \) is the time, and \( v \) is the velocity. We use the dot product because we only want to account for the flow that goes across the surface we are looking at. It is important to realize that you can only take a dot product between two vectors. This equation would make the area look like a vector. Recall that a vector has a magnitude and a direction. The magnitude of the area vector is the area of the section you are looking at. The direction is perpendicular to the surface and facing OUT. For ease we will not discuss curved surfaces. The conservation of mass holds true for mass flow rate also!

**Example:** Draw the area vectors for the following areas.

a) The area vector to the entrance to the pipe:

![Figure 12) The area vector to the entrance to the pipe.](image)

b) The area vector for the top face of each block:

![Figure 13) The area vector for the top face of each block.](image)

Notice the first two area vectors are the same length because the top areas are the same. The last one is bigger because the area at the top is bigger.
If no mass is consumed or stored by the device the conservation of mass can be written as:

\[ m_{in} = m_{out} \]

And if there is not density change, \( A \cdot v_{in} = A \cdot v_{out} \). Let’s recall enthalpy (\( h = u + RT \)). Remember that for an ideal gas \( P = pRT \) and \( RT = P/\rho \) so \( h = u + P/\rho = u + P'v' \). Here \( v' \) is NOT a derivative! It is the specific volume (\( V/m \)). Now we have defined enthalpy with energies (internal (\( u \)) and boundary work energy (\( P'v' \))) so \( m^*h \) is an energy. Therefore we can use conservation of energy on some flow problems.

Example:

Hot and cold water mixed in a mixing tank, as shown below. The hot water is at 140 K and the cold water is at 50 K. We know that \( h_1 = 100 \) J/kg, \( h_2 = 20 \) J/kg, and \( h_3 = 80 \) J/kg. Find \( m_1/m_2 \).

\[ \begin{align*}
1 & \rightarrow 2 \\
2 & \rightarrow 3 \\
3 & \rightarrow 1
\end{align*} \]

Conservation of energy: \( E_{in} - E_{out} = E_{stored} = 0 \)

\[ m_1h_1 + m_2h_2 - m_3h_3 = 0 \]

Conservation of mass: \( m_{in} - m_{out} = m_{stored} = 0 \)

\[ m_1 + m_2 - m_3 = 0 \]

\[ m_1 + m_2 = m_3 \]

back to conservation of energy

\[ m_1h_1 + m_2h_2 - (m_1 + m_2)h_3 = 0 \]
\[
\frac{m_1}{m_2} h_1 + h_2 - \left(\frac{m_1}{m_2} + 1\right)h_3 = 0
\]
\[
\frac{m_1}{m_2} (h_1 - h_3) = h_3 - h_2
\]
\[
\frac{m_1}{m_2} = \frac{h_3 - h_2}{h_1 - h_3} = \frac{80 - 20}{100 - 80} = 3
\]

Why are we using specific values for \( h \)? This is because we can look them up in a steam table. A **steam table** is a list of thermodynamic variables at various pressures and temperatures for various materials. Given \( P \) and \( T \) (along with the substance in the system) one could look up \( h, v' \) or \( u \). Also, given \( P \) and the substance one could look up \( T_{\text{sat}} \), and given \( T \) and the substance one could look up \( P_{\text{sat}} \).

**Examples:**

If you wanted to know \( h \) for super heated water vapor at a temperature of 250K and 1MPa, you could just find the appropriate table and find the information. You could also find how much effect changing the temperature has on the value you are looking for by looking at the values just below and above it.

**Super heated water vapor at 1MPa**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( v' ) (m(^3)/kg)</th>
<th>( u ) (kJ/kg)</th>
<th>( h ) (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>.20602</td>
<td>2622.3</td>
<td>2828.3</td>
</tr>
<tr>
<td>250</td>
<td>.23275</td>
<td>2710.4</td>
<td>2943.1</td>
</tr>
<tr>
<td>300</td>
<td>.25799</td>
<td>2793.7</td>
<td>3051.6</td>
</tr>
</tbody>
</table>

For any steam table information needed in class or in homework the table will be provided for you!

Now pulling everything together:

**Example:** Refrigerant enters a heat exchanger with a mass flow rate of 6kg/min. It is at 1MPa and 70 degrees C. It leaves the heat exchanger at 35 degrees C. Cooling water is used to cool the refrigerant from outside the refrigerant pipe. The water enters at
300kPa at 15 degrees C and leaves at the same pressure at 25 degrees C. There is no pressure drop anywhere in the heat exchanger. Find \( m_{\text{water}} \) if both the water is always liquid, and the refrigerant starts off as liquid and leaves as a gas.

![Diagram of heat exchanger with water and refrigerant]

\[ m_{\text{ref}} = 6 \text{ kg/min} \]
\[ T_1 = 15^\circ\text{C} \]
\[ T_2 = 25^\circ\text{C} \]
\[ T_3 = 70^\circ\text{C} \]
\[ T_4 = 35^\circ\text{C} \]
\[ P_1 = P_2 = 300 \text{ MPa} \]
\[ P_3 = P_4 = 1 \text{ MPa} \]

Conservation of Energy:
\[ m_1 h_1 = m_2 h_2 \]
and
\[ m_3 h_3 = m_4 h_4 \]
\[ m_1 h_1 + m_3 h_3 = m_2 h_2 + m_4 h_4 \]

We can find \( h_1, h_2, h_3 \), and \( h_4 \) from the steam tables because we know what state the substance is in, what the substance is, what the temperature is, and what the pressure is in all four cases.
\[ h_1 = 62.982 \text{ kJ/kg} \]
\[ h_2 = 104.83 \text{ kJ/kg} \]
\[ h_3 = 100.87 \text{ kJ/kg} \]
\[ h_4 = 303.85 \text{ kJ/kg} \]

**Conservation of Mass:**

\[ m_1 + m_3 = m_2 + m_4 \text{ for the whole system.} \]

However, because the refrigerant does not mix with the water, we can use conservation of mass just on the individual pipes so:

\[ m_1 = m_2 = m_{\text{water}} \]

\[ m_3 = m_4 = m_{\text{ref}} \]

so now putting what we have together:

\[ m_{\text{water}} h_1 + m_{\text{ref}} h_3 = m_{\text{water}} h_2 + m_{\text{ref}} h_4 \]

\[ m_{\text{water}} (h_1 - h_2) = m_{\text{ref}} (h_4 - h_3) \]

\[ m_{\text{water}} = \frac{6 \text{ kg/min} \left( \frac{303.85 - 100.87}{62.982 - 104.83} \right)}{291.1 \text{ kg/min}} \]