Lecture on Chapter 17: Energy in Thermal Processes: The First Law of Thermodynamics

One of the great conceptual breakthroughs of thermodynamics in the mid 19th-century was the realization that energy could leave or enter a system in 2 ways: mechanical work and heat. Before that, people didn't realize the connection between thermal and mechanical energy.

Heat and Internal Energy

We begin with some definitions:

- **Internal energy** E_{int} is the energy associated with the kinetic and potential energy of the atoms and molecules of a system viewed from a reference frame at rest with respect to the system. The kinetic and potential energy come from the translational, rotational, and vibrational motion of the atoms and molecules as well as from the intermolecular potential energy. For an ideal gas the internal energy is simply the kinetic energy of the particles.
- **Heat** is the energy transferred between a system and its environment because of the temperature difference between them. The amount of energy transferred is often denoted by Q. As a result of this energy transfer, the energy of the system changes.

The unit of heat is the **calorie** which is defined as the heat necessary to raise the temperature of 1 g of water from 14.5^o to 15.5^oC. The temperature is given because the amount of heat needed to raise the temperature of water by 1^oC is slightly temperature dependent. Note that 1 Calorie = 1000 calories. Calories with a capital "C" is used with regard to food. Now that we know that heat, like work, is a measure of the energy transferred to a system, we can express calories in terms of Joules:

$$1 \text{ cal} = 4.186 \text{ J} \tag{1}$$

We will typically measure heat in Joules.

Specific Heat

The amount of heat needed to raise the temperature of an object by 1^oC, say, depends on the size of an object and what material it is made of. For example, it takes a lot more heat to bring a big pot of water to a boil than a cup of water. So the amount of heat Q needed to increase the temperature of an object of mass m by a certain amount ΔT is proportional to ΔT and to m:

$$Q = cm\Delta T \tag{2}$$

where the constant of proportionality c is called the specific heat. We can rewrite this equation as follows to give the definition of c:

$$c = \frac{Q}{m\Delta T} \tag{3}$$

Notice that the specific heat is the amount of heat per unit mass that is needed to raise the temperature of a substance by an amount ΔT. We can also define a molar specific heat as the amount of heat per mole that is needed to raise the temperature of a substance by ΔT:

$$C = \frac{Q}{n\Delta T} \tag{4}$$

where n is the number of moles. The specific heat c varies from material to material. For example it takes a lot more heat to raise the temperature of a gram of water than a gram of copper by 1^oC. So the specific heat of water is much higher than the specific heat of copper.

A related term you should be familiar with is heat capacity. The **heat capacity** of an object is mc or nC. Heat capacity is proportional to the mass of an object. Qualitatively one can think of the heat capacity as a measure of the ability of the system to store energy. The more energy it can hold, the higher its heat capacity. In places of the country where it's cold in the winter, there is often a radiator in each room which has hot water circulating through it to heat the room. The radiator is usually made of metal and it's big and heavy so that it can hold lots of energy. It has a large heat capacity. If the radiator is small and doesn't have much mass, then it has a small heat capacity; it doesn't hold much energy and the room is cold.

If we add a little bit of heat dQ to the system, we change its temperature by a tiny amount dT. So we can write the specific heat as a derivative:

$$c = \frac{1}{m}\frac{dQ}{dT} \tag{5}$$

$$C = \frac{1}{n}\frac{dQ}{dT} \tag{6}$$

Note that Q is positive if heat flows into the system and negative if heat flows out.

Calorimetry

Calorimeters are instruments used to measure the specific heat of objects. To measure the specific heat c_x of an object of mass m_x, we heat it to a temperature T_x, then put it in a vessel containing some substance like water of a known mass m_w at temperature T_w. After equilibrium is reached, we measure the temperature T of the combination. Conservation of energy requires that the heat Q_{hot} leaving the hot object equals the heat entering the water:

$$Q_{cold} = -Q_{hot} \tag{7}$$

Since heat is leaving the hot object, $Q_{hot} < 0$, which means $-Q_{hot} > 0$. Eq. (7) can be rewritten as

$$m_w c_w (T - T_w) = -m_x c_x (T - T_x) \tag{8}$$

where c_w is the specific heat of water. Solving for c_x gives the specific heat of the object:

$$c_x = \frac{m_w c_w (T - T_w)}{m_x (T_x - T)} \tag{9}$$

By substituting in the known values on the right hand side, we can calculate the specific heat of the object.

Latent Heat

One of the more interesting things that happens when we heat (or cool) substances is that they change their phase. For example, ice melts or water turns into steam. These phase changes are called phase transitions and are an active area of research. In so–called first order phase transitions, such as crystal–to–liquid, latent heat is required to break the bonds between molecules and effect the phase change. For example, if you heat a crystal at a constant rate, the temperature of the crystal will rise at a constant rate until the melting temperature is reached. At that point the temperature stays constant and the heat is used to break the bonds between the molecules so that the molecules can flow and be in the liquid state. The amount of heat Q needed to melt the solid is proportional to the mass m of the crystal:

$$Q = \pm Lm \tag{10}$$

where the constant of proportionality L is called the latent heat. When heat flows into the crystal, we use the plus sign. When heat flows out of the liquid as it freezes into a crystal, we use the minus sign. The heat of fusion L_f is the term used to describe the latent heat during melting or freezing. The heat of vaporization L_v is the latent heat associated with boiling or condensing, i.e., the liquid to vapor transition. The value of the latent heat depends on the substance.

Example: This is problem 17.15. If 90.0 g of molten lead (Pb) at 327.3^{o}C is poured into a 300 g casting form made of iron (Fe) and initially at 20.0^{o}C, what is the final temperature of the system? (Assume no energy loss to the environment occurs.)

The heat leaving the molten lead goes into the iron ($Q_{Fe} = -Q_{Pb}$). As the lead cools, it solidifies, so we need to add the heat of fusion to eq. (8) which we can rewrite as

$$m_{Fe}c_{Fe}(T - T_{Fe}) = -m_{Pb}c_{Pb}(T - T_{Pb}) - m_{Pb} \cdot (-L_f) \tag{11}$$

Solve for the final temperature T:

$$T = \frac{m_{Fe}c_{Fe}T_{Fe} + m_{Pb}c_{Pb}T_{Pb} + m_{Pb}L_f}{m_{Fe}c_{Fe} + m_{Pb}c_{Pb}} \tag{12}$$

Then plug in the numbers: $m_{Pb} = 0.090$ kg, $T_{Pb} = 327.3^o$C=600.45 K, $m_{Fe} = 0.300$ kg, $T_{Fe} = 20^o$C=293.15 K, $c_{Fe} = 448$ J/kg^{o}C, $c_{Pb} = 128$ J/kg^{o}C, and $L_f = 2.45 \times 10^4$ J/kg. The specific heats come from Table 17.1 in your book, and L_f comes from Table 17.2 in your book. The final answer is $T = 59.4^o$C.

Work

The macroscopic state of a system in equilibrium is specified by macroscopic variables such as pressure, volume, temperature, and internal energy. The state of a system does not depend on its history. There are numerous ways that it could have gotten to that state. To go from one state to another, we can transfer energy to the system through heat or work. Your book calls heat and work transfer variables. We've already discussed heat. Now let's discuss work. Consider gas in a cylinder with a piston pushing down on the gas. Hold the piston fixed for a moment. Suppose the volume of the gas is V and that the gas exerts a pressure P on the piston and the walls of the cylinder. Let the area of the face of the piston be A. Now suppose we compress the gas *quasi–statically* by moving the piston so slowly that the gas remains in equilibrium at all times. If we apply a force $\vec{F}$ on the piston and move the piston a distance $(dz)\hat{k}$, then the work done on the gas is

$$dW = \vec{F} \cdot d\vec{r} = F\hat{k} \cdot (dz)\hat{k} = Fdz = PAdz \tag{13}$$

where the $+\hat{k}$ direction is downward and we used $P = F/A$ or $F = PA$. Note that $Adz = -dV$. The minus sign is because the volume shrinks and so $dV < 0$ while $Adz > 0$. So the work done on the gas is

$$dW = -PdV \tag{14}$$

If the gas is compressed, the system gains energy and $dW > 0$. $dV < 0$ so $-dV > 0$. The total work done on the gas as the volume changes from V_i to V_f is given by integrating:

$$W = -\int_{V_i}^{V_f} PdV \tag{15}$$

If we draw the path to go from the initial $(V_i,\, P_i)$ to the final (V_f, P_f) on a PV diagram, the negative of the area under the curve corresponds to the work done on the gas, provided the system moves along the curve quasi–statically. The amount of work done on the gas will depend on the path taken between the initial and final points because the area under the curve will depend on the curve in the PV plane.

Similarly the heat transferred to a system can depend on the process taken between fixed initial and final states of the system. Before we give an example of this, let's discuss the first law of thermodynamics.

First Law of Thermodynamics

We've seen that the 2 ways to transfer energy to a system is by work and by heat. So the total change in internal energy ΔE_{int} is

$$\Delta E_{int} = Q + W \tag{16}$$

This is the **first law of thermodynamics**. It is just a statement of the conservation of energy. Remember that the sign convention is such that Q is positive if heat flows into the system and negative if heat flows out. The work W done on a system is positive if the internal energy of the system increases. W is negative if work is done by the system which lowers the internal energy of the system. For an infinitesimal change in energy dE_{int} due to a tiny amount of heat dQ and due to a tiny amount of work dW being done on the system, the first law of thermodynamics becomes:

$$dE_{int} = dQ + dW \tag{17}$$

Applications of the First Law of Thermodynamics

There are a various types of processes that a system can be subjected to. Let's list them:

- In an **adiabatic process** no heat enters or leaves the system. So $Q = 0$. One way to do this is to put the system in a container whose walls are perfect thermal insulators so that no heat can enter or leave. In the real world, there are no perfect insulators but we can imagine such a system to make our calculations easier. Another way to get an adiabatic process is to perform the process very rapidly because heat exchange takes place slowly. Since $Q = 0$ in an adiabatic process, the first law becomes

  $$\Delta E_{int} = W \tag{18}$$

  So if a gas expands adiabatically, W is negative and the internal energy is lowered. If the gas is compressed adiabatically, $W > 0$ and the internal energy is increased.

- **Free expansion** is a special type of adiabatic process with both $Q = 0$ and $W = 0$. From the first law, this makes $\Delta E_{int} = 0$. So there is no change in internal energy when free expansion occurs. For an example of free expansion consider a box with perfectly insulating walls and a partition in the middle. On one side of the partition is an ideal gas and on the other side of the partition is vacuum. Now remove the partition. The gas expands to fill the whole box. This is free expansion because no heat is transferred and no work is done. The expanding gas doesn't exert any force on anything. Recall that the internal energy of an ideal gas is given by $3RT/2$. E_{int} depends only on the temperature T. Since the internal energy doesn't change in free expansion, the temperature of an ideal gas doesn't change in free expansion.

- In an **isobaric process** the pressure is kept constant ($P =$ constant). An example is an ideal gas in a cylinder with a piston that is free to move. The constant pressure is provided by the weight of the piston and the atmospheric pressure on the piston.

- In an **isovolumetric process** the volume is kept constant ($V =$ constant). As an example, imagine clamping the piston so that it cannot move. In this case no work is done ($W = 0$). So the first law gives

  $$\Delta E_{int} = Q \tag{19}$$

  So if you heat a gas in a fixed volume, all the heat goes into increasing the temperature and pressure. For example if you throw an aerosol can into the fire, the pressure and temperature of the gas in the can increase until the can explodes. (Of course, the gas does work in tearing apart the can.)

- In an **isothermal process** the temperature is held constant, though the pressure and volume may vary. For an ideal gas the internal energy $E_{int} = 3RT/2$ is solely a function of the temperature. So if T is a constant, E_{int} is a constant and the change in the internal energy is zero ($\Delta E_{int} = 0$). The first law of thermodynamics implies that

$$Q = -W \tag{20}$$

So any work done on the ideal gas leaves as heat. We can calculate the work done on an ideal gas as it moves along an isotherm (T = constant) from an initial pressure P_i and volume V_i to a final pressure P_f and volume V_f. We can use the ideal gas law $PV = nRT$ or $P = nRT/V$.

$$W = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} \frac{nRT}{V}dV = -nRT\int_{V_i}^{V_f} \frac{dV}{V} = -nRT\ln\left(\frac{V_f}{V_i}\right) \tag{21}$$

Notice that if the gas is compressed, then V_f is smaller than V_i and the ratio $V_f/V_i < 1$ which implies that $\ln(V_f/V_i) < 0$, so positive work is done on the gas ($W > 0$). Since $Q = -W$, we know how much heat leaves the system and we can write

$$Q = nRT\ln\left(\frac{V_f}{V_i}\right) \tag{22}$$

Well, that's the laundry list of processes. We can arrange these processes to form a cycle so that the system returns to the same state at the end of each cycle. So the internal energy is the same since it just depends on the state of the system, not on what has happened to it. This means that $\Delta E_{int} = 0$ and hence that $Q = -W$ after each cycle. So the net heat that enters the system goes into work. This is how a heat engine works; heat gets converted into work.

Let's look a bit closer at the first law of thermodynamics.

$$\Delta E_{int} = Q + W \tag{23}$$

The change in internal energy ΔE_{int} depends solely on the initial and final states, not on the path between them. However, the heat Q and work W do depend on the path (though the sum does not). For example a gas can go from an initial state with (V_i, P_i) to a final state (V_f,P_f) in either of 2 ways. The first way is isothermal. The gas expands slowly by pushing a piston. So the gas does work. It stays at the same temperature T_i by absorbing heat from an energy reservoir or heat bath. A heat bath or energy reservoir is considered to be a source of internal energy that is so large that a finite transfer of energy from the reservoir does not change the reservoir's temperature. The second way is by free expansion. The gas is thermally isolated with perfectly insulating walls. A partition or membrane holds the gas at its initial volume and pressure. Then the partition is removed and the gas undergoes free expansion to the final pressure and volume (V_f,P_f). No work is done ($W = 0$) and no heat is transferred ($Q = 0$), but the initial and final states are the same as that of the isothermal process. In comparing the 2 processes, we see that Q and W differ but ΔE_{int} is the same because the initial and final states are the same.

Constant volume and constant pressure molar specific heats

This difference in path or process implies that the amount of heat Q needed to produce a given temperature change ΔT will be different if we hold the volume fixed or if we hold the pressure fixed. This will produce 2 different values for the molar specific heat:

$$\begin{aligned} Q &= nC_V\Delta T \qquad \text{constant volume} && (24)\\ Q &= nC_P\Delta T \qquad \text{constant pressure} && (25) \end{aligned}$$

where C_V is the molar specific heat at constant volume and C_P is the molar specific heat at constant pressure. n is the number of moles of the substance. If we add an infinitesimal amount of heat dQ, then

$$\begin{aligned} C_V &= \frac{1}{n}\left.\frac{dQ}{dT}\right|_V \qquad \text{constant volume} && (26)\\ C_P &= \frac{1}{n}\left.\frac{dQ}{dT}\right|_P \qquad \text{constant pressure} && (27) \end{aligned}$$

where n is the number of moles.

Let us calculate C_V for an ideal gas. The volume is held fixed so no work is done. The first law of thermodynamics implies that

$$dQ = dE_{int} \tag{28}$$

The heat dQ added to the system raises the temperature of the system by an amount dT.

$$dQ = dE_{int} = \frac{3}{2}nRdT \tag{29}$$

where we used the equipartition theorem. So using eq. (26), we obtain

$$C_V = \frac{1}{n}\left.\frac{dQ}{dT}\right|_V = \frac{3}{2}R = 12.5\ \text{J/mol} - \text{K} \tag{30}$$

Notice that $C_V = 3R/2$ means that the specific heat for an ideal gas is a constant independent of temperature. This value of C_V agrees well with measurements of the constant volume molar specific heats of monatomic gases.

For a monatomic ideal gas the equipartition theorem gives $E_{int} = 3nRT/2$. The internal energy depends solely on the temperature. If we change the temperature by an amount ΔT, then the change in the internal energy

$$\Delta E_{int} = \frac{3}{2}nR\Delta T \tag{31}$$

We can express this in terms of $C_V = 3R/2$:

$$\Delta E_{int} = nC_V\Delta T \tag{32}$$

Equations (32) and (31) are true for any process in which the temperature of an ideal gas changes by ΔT, not just for processes where the volume is held fixed. These are very useful equations for an ideal gas. If you get stuck on an ideal gas problem, try using these equations.

Now let's derive an equation for C_P. When we add heat Q, eq. (24) tells us $Q = nC_P\Delta T$. When the pressure P is held constant, the volume can change and work can be done on the gas.

$$W = -P\Delta V \tag{33}$$

The ideal gas law ($PV = nRT$) implies that $P\Delta V = nR\Delta T$, so $W = -nR\Delta T$. Now let's plug this into the first law of thermodynamics:

$$\begin{aligned} \Delta E_{int} &= Q + W \\ &= nC_P\Delta T - P\Delta V \\ &= nC_P\Delta T - nR\Delta T \end{aligned} \tag{34}$$

Using eq. (32) yields

$$nC_V\Delta T = nC_P\Delta T - nR\Delta T \tag{35}$$

Cancelling out $n\Delta T$, we obtain

$$C_V = C_P - R \tag{36}$$

or

$$C_P - C_V = R \tag{37}$$

Thus,

$$C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R \tag{38}$$

This agrees with measurements on monatomic gases.

The ratio of the molar specific heats is a dimensionless quantity γ:

$$\gamma = \frac{C_P}{C_V} \tag{39}$$

For a monatomic gas,

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67 \tag{40}$$

This agrees well with experimentally measured values of γ for monatomic gases.

Specific heat of Diatomic Gases

So far we have been discussing ideal monatomic gases. What about diatomic gases in which each molecule has 2 atoms. Recall that when we talked about the equipartition theorem, we said that each degree of freedom contributes $k_BT/2$ to the average internal energy E_{int}. The translational kinetic energy has 3 degrees of freedom which contributes $3k_BT/2$. If we include the 2 rotational degrees of freedom about the 2 axes perpendicular to the line along which the diatomic molecule lies, we get an additional contribution of

$2 \times k_B T/2 = k_B T$. So translations and rotations yield $E_{int} = 5Nk_B T/2 = 5nRT/2$. This implies that

$$C_V = \frac{1}{n}\frac{dQ}{dT}\bigg|_V = \frac{1}{n}\frac{dE_{int}}{dT}\bigg|_V = \frac{5}{2}R \tag{41}$$

and

$$C_P = C_V + R = \frac{7}{2}R \tag{42}$$

If we imagine that the 2 atoms in a molecule are connected by a spring so that there is a vibrational degree of freedom, then the kinetic energy associated with vibration contributes $k_B T/2$ and the potential energy contributes $k_B T/2$ to E_{int}. Adding the translational, rotational, and vibrational degrees of freedom yields $E_{int} = 7RT/2$, $C_V = 7R/2$ and $C_P = 9R/2$.

Adiabatic Processes for an Ideal Gas

In an adiabatic process no energy is transferred by heat so $Q = 0$. So $dE_{int} = dW$. An example of an adiabatic process is one in which a gas expands or is compressed very rapidly before there is time to transfer heat. Another example is an expanding gas in a perfectly insulating container. Let us consider adiabatic processes for an ideal gas. Suppose we put the ideal gas in a container with perfectly insulating walls and allow the gas to expand. If one uses $dE_{int} = dW$, together with the ideal gas law, eq. (37) and eq. (32), then one can show that (see page 604 of Serway and Jewett):

$$PV^\gamma = \text{constant} \tag{43}$$

where $\gamma = C_P/C_V$. Contrast this with a process in which the temperature is held constant. In that case the ideal gas law implies that PV = constant. Eq. (43) implies that in terms of initial and final states

$$P_i V_i^\gamma = P_f V_f^\gamma \tag{44}$$

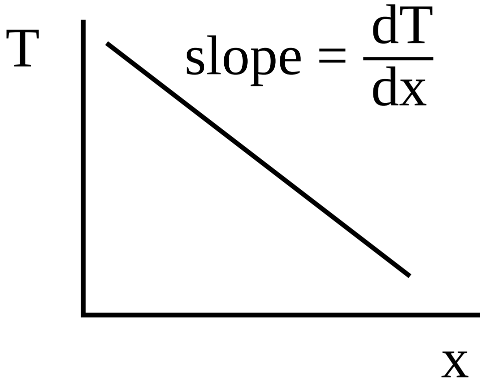
for an adiabatic process. Using the ideal gas law we can also write

$$T_i V_i^{\gamma-1} = T_f V_v^{\gamma-1} \tag{45}$$

Thermal Conductivity

When heat goes through an object, that's thermal conduction. For example when you cook soup, you put the soup in a metal pot and put the pot on the stove. The heat from the burner is conducted through the pot into the soup. Most pots are made of metal rather than glass because metal conducts heat better. We say that metal has a higher *thermal conductivity* than glass. Thermal conductivity is a measure of how well a substance conducts heat. You can think of this as energy flowing through a substance. Microscopically energy transfer occurs when hot energetic molecules with lots of kinetic energy collide with less energetic cold molecules and transfer some of their energy to the molecules with less energy. It's like standing in a crowd. If the people on one side of you start pushing and shoving, you get pushed and shoved into people on the other side of you.

To represent thermal conduction mathematically, we talk about the rate of energy transfer dQ/dt, i.e., the amount of heat that flows per unit of time. This has the units of energy per unit time or power $\mathcal{P}$. Heat flows from the hot side to the cold side. The greater the temperature difference, the faster the energy transfer, and the greater the heat flow dQ/dt. So dQ/dt will be proportional to the temperature gradient, i.e., to dT/dx. This is the slope of how the temperature changes with distance. The steeper the slope, the faster the rate of the energy transfer.



The heat flow is also proportional to the area A through which the heat is flowing because there are more "channels" to conduct the heat. This is why traffic moves faster when there are more lanes open on the freeway. Traffic crawls if there is only one lane open on the 405. So we can write

$$\mathcal{P} = \frac{dQ}{dt} \propto A\frac{dT}{dx} \tag{46}$$

The constant of proportionality is called the thermal conductivity and is denoted by κ.

$$\mathcal{P} = \frac{dQ}{dt} = \kappa A\frac{dT}{dx} \tag{47}$$

Note that the book's sign convention has $Q > 0$ when heat flows into the cold body and $Q < 0$ when heat flows out of a hot body. If you don't want to worry about the sign, just write

$$\mathcal{P} = \kappa A\left|\frac{dT}{dx}\right| \tag{48}$$

Note that objects feel colder when their thermal conductivity is higher. Remember the example of going to your car late at night? The metal exterior feels colder than the seat.