

NOTES 8: First and second law of thermodynamics.

- These are supplementary notes only, they do not take the place of reading the text book.
- Like learning to ride a bicycle, you can only learn physics by practicing. There are worked examples in the book, homework problems, problems worked in class, and problems worked in the student study guide to help you practice.

Key concepts:

1. The first law of thermodynamics is the same as the law of **conservation of energy**: The total energy of a closed system remains constant. Energy can change from one type of energy to another (for example kinetic to potential) but the total amount remains fixed.
 2. In thermodynamics energy is classified into three different types: work, W , heat, Q , and internal energy, ΔU . This allows us to write a simple form for conservation of energy (the first law of thermodynamics) as $\Delta U = Q + W$.
 3. **Heat**, Q (in Joules or calories) is a flow of energy. Objects don't have a certain amount of heat in them but energy can be added or removed. Heat transfer occurs by one of the three mechanisms of convection, conduction, radiation. Evaporation also transfers heat but since there is a mass transfer it does not usually apply to a closed system.
 4. Work is $W = \int_{x_i}^{x_f} \mathbf{F} \cdot d\mathbf{s}$ but since pressure, $P = F/A$ we can also write the work equation as $W = \int_{x_i}^{x_f} P A ds$. If we are referring to the the expansion or contraction of a gas (for example the hot gases expanding in the cylinder of a car engine) then the surface area A of a piston pushed through a distance ds results in a change of volume $dV = Ad s$ and we can write **thermodynamic work** as $W = \int_{V_i}^{V_f} P dV$ (in Joules or calories). Examples of thermodynamic work for various cases are given below. Note that on a pressure versus volume (P-V) diagram the work will be the area under the curve.
 5. **Internal energy**, ΔU , (in Joules or calories) is the sum of all of the types of energy the individual molecules have. It includes rotational energy, vibrational energy, chemical potential energy and kinetic energy (average kinetic energy by itself is proportional to temperature; $3/2 k_B T = \langle 1/2 m v^2 \rangle$). Chemical potential energy is the energy absorbed or released by chemical reactions between molecules.
 6. In an **ideal gas** the molecules are non interacting point particles and so do not have rotational, vibrational or chemical potential energy. The only kind of energy an ideal gas can have is kinetic energy (temperature).
 7. Note that the first law of thermodynamics tells us energy is conserved but does not provide any restrictions about how energy may be converted from one type to another.
1. The **second law of thermodynamics** restricts the kinds of energy transfers that are possible in a closed system.
 2. The second law also determines the theoretical efficiency of some kinds of energy transfers. **Efficiency** is defined to be $e = E_{out}/E_{in} \times 100\%$ where E_{out} is the output energy or work done by a process and E_{in} is the input energy (or work) needed to make the process occur.
 3. There are several different ways of stating the second law. Although it might not be obvious at first glance, each different statement of the second law can be used to prove the others.
 4. Version **one** of the second law: Entropy (another word for disorder) increases. (see below for explanations)

5. Version **two** of the second law: In a closed system heat flows from hot to cold, it takes input energy to make it flow the other way. (see below for explanations)
6. Version **three** of the second law: The Carnot cycle is the most efficient cycle possible for a process that involves heat transfer: $e = (1 - T_2/T_1) \times 100\%$. (see below for explanations)
7. A **heat engine** is a device that converts heat into mechanical work. Because a heat flow is needed for a heat engine to operate, some energy has to flow out of the system and this outflow cannot be converted into mechanical work (this is sometimes called 'waste heat'). Heat engines can never convert 100% of the input energy into useful mechanical work. This limitation is a consequence of the second law, there is no way to avoid it.
8. One consequence of the second law is that it is not possible, even in theory, to make a heat engine which is 100% efficient. For example, gasoline engines must have a radiator or cooling fins where heat is expelled to the environment. Current gasoline engines are only about 25% efficient as a result (75 cents on the dollar goes to heating the air outside the car). The second law says we can do a little better (the Carnot cycle) but never 100%, even if all friction is eliminated.
9. This also means that it is impossible to do something like extract heat from the ocean to do mechanical work. You must have a cool reservoir to expel waste heat to and there isn't a convenient one available.
10. It is possible to use the so called 'waste heat' from a heat engine in other ways. For example in the winter time the waste heat from your car engine can be used to warm the people in the car. Factories and electric generating plants which operate heat engines can sometimes sell or otherwise use the waste heat (for example for heating homes) making the overall efficiency of the combined processes more efficient.
11. Other devices such as fuel cells, batteries and electric engines are not limited in efficiency by the second law because they are not heat engines, they do not convert heat energy into mechanical work (they perform other kinds of energy conversions).

Applications and examples done in class, on quizzes, etc:

Version one of the second law: Entropy increases.

Suppose we have three coins and want to know how many different results we could get from tossing them. Here are all the possibilities:

coin	Toss 1	Toss 2	Toss 3	Toss 4	Toss 5	Toss 6	Toss 7	Toss 8
1	H	H	H	H	T	T	T	T
2	H	H	T	T	H	H	T	T
3	H	T	T	H	T	H	H	T

From the results we can see that there is only one way to have all heads but three ways to have two heads and one tail. Our conclusion is that getting a result of two heads and one tail is three times more likely than all heads or all tails.

What does this have to do with thermodynamics? Suppose we have three molecules which can go randomly into two sides of a container. Let's call the left side T and the right side H! Using the same reasoning we can see that it will be three times more likely to find two molecules in the H side and one in the T side than it is to find all three in the H side. In other words it is much more probable that molecules will spread out in roughly equal numbers between the two sides of the container because there are more ways to have that happen.

Probability theory tells us what results to expect in these kinds of situations. Theory says the probable number of heads, $P(H)$, in a coin toss with N coins is given by $P(H) = N/2 \pm N^{1/2}$ with a 93% confidence limit. Lets calculate this probability for a few values of N .

N	$P(H) = N/2$	$\pm N^{1/2}$	% error = $N^{1/2}/N \times 100\%$
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100	50	10	10%
1000	500	31.6	3.2%
10000	5000	100	1.0%
100000	50000	316.2	0.3%
1000000	500000	1000	0.1%
10000000	5000000	3162.2	0.03%
100000000	50000000	10000	0.01%
1000000000	500000000	31622.8	0.003%

Look what happens as the number of coins increases! If you guess you will get 500,000 heads when tossing 1,000,000 coins you only expect to have an error of 0.1%! In other words for large numbers of coins you expect to be very close to exactly half heads and half tails as compared to small numbers of coins where you occasionally do get all heads or all tails.

What does this have to do with thermodynamics? Let's think about putting molecules in a box again. Generally the number of molecules in a container is quite large; a mole (6.02×10^{23} atoms) is a typical quantity. Applying the discussion of the coin toss we see that the error in assuming a mole of molecules is equally divided between the two sides of the container ($N/2$ in each side) is very small. Or stated a different way, it is very unlikely (very small error) that we find that the molecules are NOT divided equally between the two sides.

The number of different ways a particular outcome can occur is called the **number of microstates**, Ω . So for the case of three coins $\Omega = 1$ for all heads or all tails because there is only one way to have this occur so only one microstate available but $\Omega = 3$ for two heads and one tail because there are three ways for this to occur so there are three microstates. **Entropy** is defined to be $S = k_B \ln(\Omega)$ where k_B is Boltzman's constant ($k_B = 1.38 \times 10^{-23}$ J/K) and \ln is the natural logarithm. Notice the units for entropy will be Joules per Kelvin.

Now we see something interesting. Notice that the entropy for all heads is lower than the entropy for the case of two heads and one tail. In our three coin toss the entropy for all heads is $k_B \ln 1 = 0$ while the entropy for two heads and one tail is $k_B \ln 3 = 1.5 \times 10^{-23}$ J/K which is larger than 0. So another way to state the fact that getting half heads in a coin toss of N coins is more likely than some other distribution (two heads and one tail for example) is to say that the outcome with the highest entropy is more likely. States with higher entropy are more likely than states with low entropy. This is a statement purely based on the laws of probability.

We can also see that, as the numbers of coins (or molecules in a container) gets larger the state with the highest entropy becomes almost certain (the error gets VERY small). For a mole of molecules we can say with near certainty that the system will be in the state of highest entropy. This is a result purely due to probability applied to large numbers of molecules.

It is possible to make a loose connection between **entropy and disorder**. If all of the molecules are on one side of the box then we have more information about where they are than if half is on each side. They are less disordered if they have a specific arrangement (all on one side) than if half is on each side. Closed systems tend towards an increase in disorder. For example, living organisms are a ordered systems because they use energy (they are not closed systems). If there is no energy flow into the system the organism will die and decay into disorder.

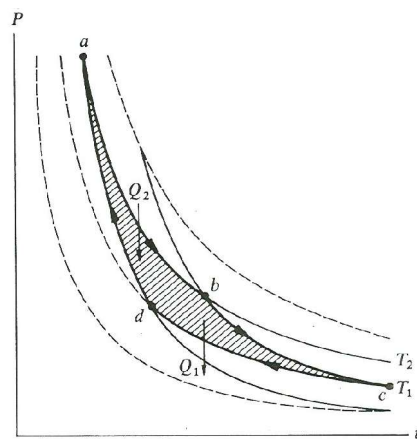
Version two of the second law: In a closed system heat flows from hot to cold, it takes input energy to make it flow the other way.

Consider two containers of gas (H and T) which are at different temperatures and the same two containers sometime later with the same temperature. In the first case we have more information about the distribution of kinetic energy (more is in the hot container) whereas in the second case we have less information (we don't have information about where the kinetic energy is).

The first case has a lower entropy than the second case. So if we were to put a hot and cold container in thermal contact they would tend to go towards the more disordered state and arrive at the same temperature.

Version three of the second law: The Carnot cycle is the most efficient cycle for a process that involves heat transfer.

1. In engineering applications we are interested in processes where the system ends up in the same state by going through a cycle that repeats. For example the piston in a car engine goes through a cycle of intaking a fuel/air mixture, burning the mixture, expansion of the burning gases to provide a force and work and then finally expelling the burnt fuel/air mixture. In a cyclic process the eternal energy change, $\Delta U = 0$ since the process eventually returns to its original state. The first law then becomes $Q = W$; the work done is determined by the heat flow.
2. A process is said to be **quasistatic** if at any point we could stop and go back to the previous state. An example is lifting or lowering a mass very slowly (imagine a system of pulleys and balance weights as opposed to just dropping the mass).
3. A thermodynamic process is said to be **reversible** if it is quasistatic and no energy is lost to friction. Popping a balloon is not reversible because it isn't quasistatic. Pistons in the real world are not reversible because there is friction. **Isothermal** (constant temperature) and **adiabatic** (no heat flow) expansion are two examples of reversible processes.
4. The engineer Sadi Carnot proved that there is one type of cyclical process which beats all others in efficiency. The Carnot cycle has the maximum theoretical efficiency possible in a heat engine (a heat engine is a device that turns heat into mechanical energy). It is the most efficient because all of the steps are reversible (quasistatic and no friction).
5. Here are the steps of the Carnot cycle (P versus V graph shown below).
 1. Isothermal expansion (point a to point b in graph): Absorb heat Q_2 at constant temperature T_2 by letting the piston expand while in contact with a large reservoir with fixed hot temperature.
 2. Adiabatic expansion (point b to point c in graph): Thermally isolate the piston and let it continue to expand to P_c and V_c . No heat exchange.
 3. Isothermal cooling (point c to point d in graph): Remove heat Q_1 at constant temperature T_1 by letting the piston expand while in contact with a large reservoir with fixed cool temperature.
 4. Adiabatic contraction (point d to point a in graph): Thermally isolate the piston and let it continue to contract back to P_a and V_a . No heat exchange.



6. The work done (area under the curve) for the four steps are worked out below in the supplemental material. The result is that the net work done depends only on the heat flow during the isothermal processes. The work done for a Carnot cycle is thus $W_{\text{total}} = Q_2 - Q_1$.
7. Also using arguments shown below we have that $Q_1/T_1 = Q_2/T_2$. This allows us

to write the efficiency of a Carnot cycle as: $e = W_{\text{total}} / Q_1 = (Q_2 - Q_1) / Q_2 = 1 - Q_1 / Q_2$. Using the first expression allows us to write the **efficiency of a Carnot cycle** as $e = (1 - T_1/T_2) \times 100\%$ where T is in Kelvin.

- Notice that the efficiency of the most efficient heat engine depends only on the temperatures of the hot (T_2) and cold (T_1) reservoirs. So the only way to make an engine more efficient is to either burn fuel at a hotter temperature or lower the outside temperature.

Supplementary material

- The work done in the Carnot cycle is the area inside the P-V diagram. We can get this by finding the area (integral) under each of the separate steps.
- Using the ideal gas law $PV = nRT$ we can show that for an isothermal process

$$W_{a \rightarrow b} = Q_2 = \int_{V_a}^{V_b} PdV = \int_{V_a}^{V_b} \frac{nRTdV}{V} = Nk_B T_2 \ln\left(\frac{V_b}{V_a}\right) \text{ likewise}$$

$$W_{c \rightarrow d} = Q_1 = - \int_{V_c}^{V_d} PdV = -Nk_B T_1 \ln\left(\frac{V_c}{V_d}\right) .$$

- Your book shows that for an adiabatic process $PV^\gamma = k$ where γ is the ratio of specific heat at constant pressure to the specific heat at constant volume and k is a constant. Using this in our definition of work gives

$$W_{b \rightarrow c} = \int_{V_b}^{V_c} PdV = \int_{V_b}^{V_c} kV^{-\gamma} dV = \frac{k}{-\gamma+1} (V_c^{-\gamma+1} - V_b^{-\gamma+1}) \text{ likewise}$$

$$W_{d \rightarrow a} = \int_{V_d}^{V_a} PdV = \int_{V_d}^{V_a} kV^{-\gamma} dV = \frac{k}{-\gamma+1} (V_a^{-\gamma+1} - V_d^{-\gamma+1}) .$$

- Using the ideal gas law and the fact that $k = PV^\gamma$ we can replace the k to get

$$W_{b \rightarrow c} = \frac{P_b V_b}{-\gamma+1} \left(\left(\frac{V_b}{V_c}\right)^{\gamma-1} - 1 \right) = nRT \left(\left(\frac{V_b}{V_c}\right)^{\gamma-1} - 1 \right) \text{ with a similar expression}$$

for $W_{d \rightarrow a}$.

- Your book also shows that for an adiabatic process $TV^{\gamma-1} = \text{constant}$ so $T_2 V_b^{\gamma-1} = \text{constant} = T_2 V_c^{\gamma-1}$ and $T_1 V_d^{\gamma-1} = \text{constant} = T_1 V_a^{\gamma-1}$. Dividing these pairs of

equations leads to: $\frac{V_b}{V_a} = \frac{V_c}{V_d}$. Replacing the ratios in the work equation for

adiabatic work shows that the net work done in the two adiabatic processes cancel out so that the work done in the entire cycle depends only on the two isothermal processes, as promised for a reversible cycle.

- Using the ratio of volumes in the isothermal expressions for work shows that

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} . \text{ This ratio was important in establishing the efficiency of the}$$

Carnot cycle.

- Originally entropy was defined to be $S = Q/T$ (long before microstates). It can be shown that the two definitions are equivalent.

The connection between the first and third statements of the second law.

First off, reversible cyclic processes have to result in no change of entropy for the engine. We end up in the same place we started from so the disorder has neither increased nor decreased for the engine. So far so good. Now let's imagine using this cyclic engine and only a hot reservoir (the ocean for example) with no cool reservoir. Well the hot reservoir would lose entropy (become more ordered) in this process since heat flows out of it ($S = Q/T$ is a negative quantity). But according to the first (disorder) version of the second law the overall, total entropy has to increase. The only way to get entropy to increase overall for this process (or even to remain constant) is to raise the entropy somewhere other than the hot reservoir or the engine. In other words you have to raise the entropy

(increase disorder) of a cool reservoir somewhere else. But this is saying the same thing as version three of the second law: if the process is cyclic we've got to have waste heat exhausted to a cool reservoir somewhere in the process. So all versions of the second law give the same results.