CHE 260 Lecture Notes

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CHE260

The up-to-date version of this document can be found at https://github.com/HaysonC/skulenotes

"If there is one word that describes this class it would be energy."

Chapter 1

Thermodynamics

Systematic Approach to Problem Solving in Thermodynamics

You should adopt a systematic approach when tackling problems to avoid getting confused by a lot of information. The following steps are helpful:

- 1. **Find.** Read the problem and state what you are asked to find in your own words. This step may seem obvious, but it is surprising how often people misunderstand the question or miss essential information.
- 2. **Known.** List all the information and properties provided, as well as information about properties that remain constant (e.g. the volume in a isochoric process or the temperature in an isothermal process).
- 3. **Diagrams.** Draw a schematic diagram of the system. Mark the system boundary and decide whether the system is a control mass or volume. Show energy and mass transfers between the system and surroundings by arrows. Draw a process diagram if necessary.
- 4. **Assumptions.** Decide how you are going to model the system. List all assumptions that you make.

- 5. **Governing Equations.** Which conservation law are you going to apply? Depending on what you are trying to find, you may use principles of conservation of mass or energy. Write down the governing equations.
- 6. **Properties.** List all property values that are not given in the problem statement. This includes information extracted from tables or other sources.
- 7. **Solution.** Substitute known values of variables in the governing equations and solve them to find unknowns.
- 8. **Answer.** State the answer and confirm that it is what was asked for.
- 9. **Discussion.** Are your results reasonable? Can you draw any conclusions from them?

1.1 Systems and Properties in Thermodynamics

Definition 1.1.0.1 (Energy). You should have learned that energy is the ability to do work.

Definition 1.1.0.2 (Work). You also learned that work is the transfer of energy.

We have a problem. The above two definitions are in terms of each other. This touches on the theory of fundamental concepts:

Fundamental Concepts For example, the following are fundamental concepts in physics:

- Time
- Mass Interestingly, we don't measure mass directly; instead, we measure weight, which is the force exerted by gravity on an object, and from that we deduce mass.
- Space

In this course, we are going to explore two:

- Energy Energy is pretty familiar to us.
- Entropy Entropy is what gives students the most trouble; you can't show someone a picture of entropy, it is abstract.

These fundamental concepts are in arbitrary units and form the foundation 'axioms' in science.

1.1.1 Energy

Energy An understanding of energy is its ability to **lift weights**. This is a way we could test if there is energy.

Example 1.1.1.1 (Potential Energy). A 1 kg mass lifted 1 meter has a potential energy of about 10 J. Imagine that it is attached to a balance, with a small mass on the other side, then, it is able to lift that weight.

Example 1.1.1.2 (Kinetic Energy). Given a flying ball that hits a lever with a mass rested on it, given the appropriate angle, the ball can transfer its kinetic energy to the mass, causing it to lift.

Example 1.1.1.3 (Heat). Given a gas in a container, if we heat the gas, it expands and lifts objects on top of it.

Example 1.1.1.4 (Newcomen Engine). The above example is actually a simplified representation of how the Newcomen engine operates. In the Newcomen engine, steam is used to create a vacuum that lifts a piston, demonstrating the conversion of thermal energy into mechanical work.

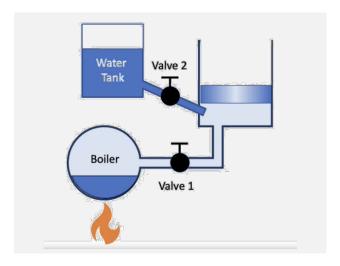


Figure 1.1: A Newcomen Engine

When Valve 1 opens, steam fills the chamber and lifts up the piston. When Valve 2 opens (with valve 1 closes), water gets sprayed, evaporates, and condenses, causing the piston to lower.

However, the Newcomen engine is not the most efficient steam engine, most heat is lost in the heating and cooling process. Solution? A external condenser was added to improve efficiency by cooling the steam and creating a vacuum, allowing the piston to be pulled down more effectively. This is the **Watt Engine**.

Steam Cycle The steam cycle is a thermodynamic cycle that converts heat energy into mechanical work. It consists of four main processes:

- 1. **Heating** The working fluid (steam) is heated in the boiler, converting water into steam and increasing its energy.
- 2. **Expansion** The high-pressure steam expands in the piston, doing work on the piston and converting thermal energy into mechanical work.
- 3. Cooling The steam is cooled in the condenser, releasing heat to the surroundings and condensing back into water.
- 4. Compression The water is pumped back into the boiler, completing the cycle.

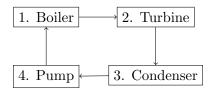


Figure 1.2: Steam Cycle Diagram

Definition 1.1.1.5 (Heat Engine). A heat engine is a device that converts thermal energy into mechanical work. It operates by taking in heat from a high-temperature source, performing work using that heat, and then releasing some waste heat to a low-temperature sink. The steam engine is a classical instance of a heat engine.

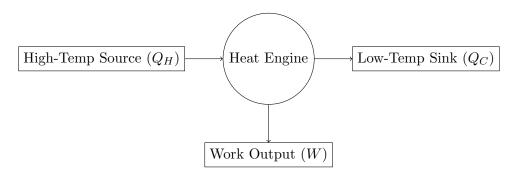


Figure 1.3: A Heat Engine

Efficiency of a Heat Engine The efficiency of a heat engine is defined as the ratio of the work output to the heat input:

$$\eta = \frac{W}{Q_H} \tag{1.1}$$

Obviously, the best engine is when η is maximized (W is maximized, and Q_H is minimized). For example, a Newcomen engine has a low efficiency ($\eta \approx 0.34\%$), while a classic watt engine has a higher efficiency ($\eta \approx 4\%$). The modern powerplant is optimized such that it has $\eta \approx 30\%$.

This begs the question, can we create a heat engine with 100% efficiency (i.e., $Q_C = 0$)? The answer is no, due to the second law of thermodynamics [Sadi Carnot (1830)]. For now, consider the wasted energy Q_c .

Irreversibility and Spontaneity The process of losing heat is spontaneous and irreversible. Once heat is lost to the cooler surroundings, it cannot be completely recovered and converted back into work, however, the process of bringing heat from a cooler body to a hotter body is non-spontaneous and requires external work (e.g., a refrigerator). These give rise to the concept of irreversibility in thermodynamic processes, from the laws of thermodynamics.

The first law of thermodynamics is simple and easy to understand:

Definition 1.1.1.6 (First Law of Thermodynamics). The first law of thermodynamics states that energy cannot be created or destroyed, only transformed from one form to another. In the context of a heat engine, this means that the work output (W) is equal to the heat input (Q_H) minus the heat rejected (Q_C) :

$$W = Q_H - Q_C \tag{1.2}$$

The second law formalizes the concept of the directionality of thermodynamic processes, stating that heat cannot spontaneously flow from a colder body to a hotter body. This law introduces the idea of entropy, a measure of the disorder or randomness in a system, which tends to increase over time in isolated systems.

Definition 1.1.1.7 (Second Law of Thermodynamics). The second law of thermodynamics states that the total entropy of an isolated system can never decrease over time. We consdier entropy as:

$$S = \frac{Q}{T} \tag{1.3}$$

In the above example, we can see that entropy increases as heat is transferred from the hot reservoir to the cold reservoir:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = \frac{Q_C}{T_C} - \frac{Q_H}{T_H} > 0 \tag{1.4}$$

Since $Q_C = Q_H$ in a closed system and $T_H > T_C$, we have $\Delta S > 0$.

1.1.2 Systems and States

Definition 1.1.2.1 (System). Any piece of matter or a region of space.

Definition 1.1.2.2 (Boundary). The boundary is the surface that separates the system from its surroundings. It can be real or imaginary, fixed or movable, and can allow or prevent the transfer of mass and energy.

Types of Systems There are three main types of systems: closed, open, and isolated. Defined as the following:

Definition 1.1.2.3 (Closed System/Control Mass). A closed system is one where mass cannot cross the boundary, but energy can. An example of a closed system is a sealed container of liquid, or a bag of gas, where we can do work on it.

Definiton 1.1.2.4 (Open System/Control Volume). An open system is one where both mass and energy can cross the boundary. An example of an open system is a flowing pipe, or a car engine, where mass (water, air) and energy (heat, work) can enter and leave the system.

Definiton 1.1.2.5 (Isolated System). An isolated system is one where neither mass nor energy can cross the boundary. An example of an isolated system is a thermos bottle that is perfectly insulated from its surroundings.

Definition 1.1.2.6 (Property). A property is any attribute of a system that can be measured without knowing the history of the system.

(Example) Position, Temperature, Mass, Energy

(Non-example) Work, Transfer of energy (heat), Mass outside the system (denote δm)

$$W = \int dW \quad \text{(depends on path)} \tag{1.5}$$

Hence, to remind ourselves, we denote infinitesimal work as δW instead of dW. Then, we can compute the work done by the force field ${\bf F}$ along a curve C as:

$$\delta W = \int_C \mathbf{F} \cdot ds \tag{1.6}$$

Here's a quick refresher on line integrals and basic math:

Example 1.1.2.7 (Computing work). The force acting on a 5 kg object varies with time as F = (50 + 10t) N, where t is the time in seconds. If the body starts from rest, how much work is done on it in 10 s?

The object is travelling for a straight line, so we can simply parametrize the curve as ds = vdt = r'dt. We can compute the velocity v by integrating the acceleration a = F/m. Firstly the work is given by:

$$W = \int_C F \cdot ds = \int_0^{10} F \cdot v dt$$

Since they are in the same direction, we can treat them as scalars. Now, we compute v:

$$v = \int_0^t a dt = \int_0^t \frac{F}{m} dt = \int_0^t \frac{50 + 10t}{5} dt = 10t + t^2 + (C = 0 : object starts from rest)$$

Hence, we have:

$$W = \int_0^{10} (50 + 10t)(10t + t^2)dt = 100\,000 \text{ J}$$

Intensive and Extensive Properties Properties can be classified into two categories: intensive and extensive.

Definition 1.1.2.8 (Extensive Property). An extensive property is one that depends on the size or extent of the system.

(Example) Mass, Volume, Energy

Definition 1.1.2.9 (Intensive Property). An intensive property is one that does not depend on the size or extent of the system.

(Example) Temperature, Pressure, Density

We can convert any extensive property to an intensive property by dividing it by mass or volume. For example, specific volume v or specific energy u:

$$v = \frac{V}{m}, \quad u = \frac{U}{m}$$

Definition 1.1.2.10 (State). The state of a system is defined by its properties at a specific moment in time. A state is a condition of the system that can be described by a set of properties. For example, the state of an ideal gas can be described by its pressure, volume, and temperature.

Definition 1.1.2.11 (Steady State). A system is in steady state if its properties do not change with time. In other words, the system is in a state of equilibrium, and there are no net changes in mass or energy within the system.

(Example) An overflowing bucket of water, in which case the system is unchanging but interacting with its surroundings.

Definition 1.1.2.12 (Equilibrium). An **ISOLATED** system is in equilibrium if its properties are uniform throughout the system and do not change with time (constant).

(Example) A gas in a closed container that has been left undisturbed for a long time.

Example 1.1.2.13. Consider a gas in a cylinder with a movable piston. If the piston is held in place, the gas is in a steady state, as its properties (pressure, volume, temperature) do not change with time. However, if the piston is allowed to move, the gas will expand or compress, and its properties will change with time, indicating that it is not in a steady state.

Definition 1.1.2.14 (Process). A process is a transformation from one state to another. A process can be described by the path taken by the system in the property space. For example, a gas can undergo a process of compression or expansion, which changes its pressure, volume, and temperature.

1.1.3 Modeling Ideal Gas

Definition 1.1.3.1 (Quasi-Equilibrium Process (Reversible Path)). A quasi-equilibrium process is a process that occurs slowly enough that the system remains in a state of equilibrium at all times. In other words, the properties of the system change so (infinitely) slowly that they can be considered constant during the process. In this case, this path is reversible.

(Example) A gas in a cylinder with a movable piston that is compressed or expanded very slowly, allowing the gas to remain in equilibrium throughout the process.

Definiton 1.1.3.2 (Real Process (Irreversible Path)). A real process is a process that occurs at a finite rate, and the system may not remain in a state of equilibrium at all times. In other words, the properties of the system may change rapidly during the process, and the system may not be able to adjust to these changes quickly enough to maintain equilibrium. In this case, this path is irreversible.

(Example) A gas in a cylinder with a movable piston that is compressed or expanded quickly, causing the gas to deviate from equilibrium during the process. In that process, the work done is more than that of a quasi-equilibrium process.

Motivation We care about this because this is the process in which we ignite an engine, allowing gas to expand rapidly, pushing the piston down and doing work.

Definition 1.1.3.3 (Ideal Gas Model). Consider an isolated system with molecules that:

- Have negligible volume compared to the volume of the container. (point mass)
- Do not interact with each other except during elastic collisions.
- Are in constant random motion without spin or vibration.

The best example of this is a noble gas (e.g., helium, neon, argon). Since they are inert and monoatomic. For all we care about in this course all gas are ideal unless:

- They are at very high pressure (Condier more than 1 atm).
- They are at very low temperature (Consider close to 0 K).

Such a system is called an ideal gas. The macroscopic observation of pressure is the average force per unit area exerted by the gas molecules colliding with the walls of the container, so if we increase the number of molecules or decrease the volume, the pressure increases proportionally, this is Boyle's law:

Definition 1.1.3.4 (Boyle's Law). For a given amount of gas at constant temperature, the pressure of the gas is inversely proportional to its volume:

$$P \propto \frac{1}{V} \quad \Rightarrow \quad PV = \text{constant}$$
 (1.7)

where N is the number of molecules. We can proof the PV inverse relationship a momentum conservation argument. Consider linear path with length L, since collisions are elastic, the change in momentum for each collision is $\Delta p = 2mv_x$. The time between collisions is $\Delta t = \frac{2L}{v_x}$, so the force exerted on the wall is:

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{\frac{2L}{r}} = \frac{mv_x^2}{L}$$

The pressure is then given by:

$$P = \frac{F}{A} = \frac{mv_x^2}{AL} = \frac{mv_x^2}{V}$$

Thus, we have $PV \propto mv_x^2$. Now, define the RMS velocity as $v_{rms} = \sqrt{\frac{1}{N}\sum_{i=1}^N v_i^2}$, and consider random motion, we have $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}v_{rms}^2$. Hence, we have:

$$PV \propto Nm\overline{v_x^2} = \frac{1}{3}Nmv_{rms}^2$$

where Nm is the total mass of the gas. Then, we complete the argument of the gas moving in all direction.

Example 1.1.3.5 (Boyle's Law). Consider a gas in a cylinder with a movable piston. If we compress the gas by pushing the piston down, the volume of the gas decreases, and the pressure increases. This relationship is described by Boyle's law, which states that for a given amount of gas at constant temperature, the pressure of the gas is inversely proportional to its volume:

We can also observe that increasing the temperature increases the average kinetic energy of the molecules, which increases the frequency and force of collisions with the walls of the container, leading to an increase in pressure, this is Charles's law:

Definition 1.1.3.6 (Charles's Law, Total Internal Energy). For a given amount of gas at constant volume, the pressure of the gas is directly proportional to its absolute temperature:

$$P \propto T$$
 (1.8)

And the total internal energy of an ideal gas is the sum of the kinetic energies of all the gas molecules, which is also directly proportional to its absolute temperature:

$$U = \frac{3}{2}Nk_BT = \frac{3}{2}nR_uT (1.9)$$

U is a extensive property, so it is proportional to the number of molecules N (or moles n). The intensive property is the specific internal energy:

$$u = \frac{U}{m} = \frac{3}{2} \frac{R_u}{M} T = \frac{3}{2} RT \tag{1.10}$$

where M is the molar mass of the gas, and

$$R = \frac{R_u}{M} \tag{1.11}$$

is the specific gas constant.

This is a consequence of the kinetic theory of gases, which model temperature as the average kinetic energy of the gas molecules, so we have:

$$\frac{1}{2}mv_{rms}^2 = \frac{3}{2}R_uT$$

Dividing by N_A (Avogadro's number), and define the boltzmann constant $k_B = \frac{R_u}{N_A}$, we have:

$$\frac{1}{2}m_e v_{rms}^2 = \frac{3}{2}k_B T$$

We multiply both sides by N (number of molecules), and substitute into the previous equation, we have:

$$\frac{1}{2}m_e v_{rms}^2 N = \frac{3}{2}k_B T N$$

The above is the internal energy of the gas. Thus, we can deduce the following Ideal Gas Law, which matches macroscopic observations:

Definition 1.1.3.7 (Ideal Gas Law). Consider the combination of Boyle's and Charles's law, we have the ideal gas law:

$$PV = nR_u T = mRT \tag{1.12}$$

where $R_u = 8.314 \,\mathrm{J/(mol~K)}$ (or, equivalently, $R_u = 8 \times 10^3 \,\mathrm{J/(kmol~K)}$) is the universal gas constant, and n is the number of moles of gas. $R = \frac{R_u}{M}$ is the specific gas constant, where M is the molar mass of the gas.

Example 1.1.3.8. A spherical balloon with $d = 6 \, m$ is filled with helium gas at $P = 200 \, kPa$ and $T = 20^{\circ}C$. Calculate the mass and number of moles of helium in the balloon. (Assume ideal gas behavior).

We can use the ideal gas law to solve this problem. First, we need to calculate the volume of the balloon:

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (3)^3 = 113.1 \,\mathrm{m}^3$$

Next, we can use the ideal gas law to calculate the number of moles of helium in the balloon:

$$n = \frac{PV}{R_u T} = \frac{200 \times 10^3 \times 113.1}{8.314 \times (20 + 273)} = 9280 \,\text{mol}$$

Finally, we can calculate the mass of helium in the balloon using the molar mass of helium (M = 4 g/mol):

$$m = nM = 9280 \times 4 = 37120 \,\mathrm{g} = 37.12 \,\mathrm{kg}$$

Example 1.1.3.9 (Adiabatic Compression). Consider an ideal gas undergoing adiabatic compression¹. Since no heat is exchanged with the surroundings (Q = 0), the work done on the gas increases its internal energy, which raises the temperature. Using the adiabatic relations,

$$PV^{\gamma} = \text{constant}, \quad TV^{\gamma-1} = \text{constant},$$

we see that a decrease in V leads to an increase in both P and T.

Example 1.1.3.10 (Isothermal Expansion). Consider an ideal gas undergoing isothermal expansion². Since the temperature remains constant ($\Delta T = 0$), the internal energy of the gas does not change ($\Delta U = 0$). The work done by the gas during expansion is equal to the heat absorbed from the surroundings (Q = W). Using the ideal gas law, we can see that as V increases, P decreases, while T remains constant.

Note For all ideal gas processes, the internal energy U depends only on temperature T, not on pressure P or volume V. This is a key property of ideal gases and simplifies the analysis of thermodynamic processes involving them.

Definition 1.1.3.11 (Change in Internal Energy). The change in internal energy of an ideal gas can be calculated using the specific heat capacity at constant volume (c_v) :

$$\Delta U = \frac{3}{2}mk_B\Delta T = mc_v\Delta T \tag{1.13}$$

¹This differs from **isothermal** compression, where the temperature remains constant.

²This differs from **adiabatic** expansion, where no heat is exchanged.

1.2. FIRST LAW OF THERMODYNAMICS

where c_v [J kg⁻¹ K⁻¹] is the specific heat capacity at constant volume. For a monoatomic ideal gas, we have:

$$c_v = \frac{3}{2}R\tag{1.14}$$

where R is the specific gas constant.

Example 1.1.3.12. How much energy is required to heat 10kg of air with 20°C at 1 bar to 120° at constant volume? What is the final pressure? (Assume ideal gas behavior, and $c_{v,air} = 0.717 \ kJ/kg \ K$)

Consider the change of internal energy:

$$\Delta U = mc_v \Delta T = 10 \times 100 \times c_{v,air} = 1000 \times 0.717 = 717 \,\text{kJ}$$

Now consider the change of pressure, we first isolate for the control:

$$\frac{mR}{V} = \frac{P}{T}$$

So we can compute the final pressure:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow P_2 = P_1 \frac{T_2}{T_1} = 1 \times \frac{393}{293} = 1.34 \,\text{bar}$$

1.2 First Law of Thermodynamics

Motivation We want to understand how energy is conserved in a system, and how energy is transferred between a system and its surroundings. This is important for understanding how engines work, how to design efficient systems, and how to analyze thermodynamic processes.

The same definition as before 1.1.1.6.

Definition 1.2.0.1 (First Law of Thermodynamics for a Closed or Isolated System). For a closed system, the energy balance can be expressed as:

$$\Delta E_{in} - \Delta E_{out} = \Delta E_{system} \tag{1.15}$$

where ΔE_{in} is the energy entering the system, ΔE_{out} is the energy leaving the system, and ΔE_{system} is the change in energy of the system. The total energy of the system can be expressed as:

$$E_{system} = U + KE + PE \tag{1.16}$$

where U is the internal energy, KE is the kinetic energy, and PE is the potential energy.

Sign Convention Relative to a system, we adopt the following sign convention:

- Energy transfer to the system is positive.
- Energy transfer from the system is negative.

Definiton 1.2.0.2 (Energy Transfer from a System). The energy transfer from a system can occur in two ways: heat transfer (Q) and work transfer (W). The first law of thermodynamics can be expressed as:

$$dE = \delta Q + \delta W \tag{1.17}$$

Dividing by dt, we have the rate form of the first law:

Definition 1.2.0.3 (Rate Equation of the First Law of Thermodynamics).

$$\frac{dE}{dt} = \dot{Q} + \dot{W} \tag{1.18}$$

where \dot{Q} is the rate of heat transfer, and \dot{W} is the rate of work transfer.

1.2.1 Work Modes

Definition 1.2.1.1 (Boundry Work). Force acts on the boundries of a systems and deformes them. (Example) Expansion and compression of a gas

Assuming for a Quaso-equilibrium process, and no friction, we can compute the boundary work as:

$$\delta W = Fdx = PAdx = -PdV \tag{1.19}$$

where P is the pressure of the gas, A is the area of the piston, and dx is the displacement of the piston. The negative sign is because when the gas expands, it does work on the surroundings, so the work done by the system is negative. Also, we can consider the total work by:

$$w_{12} = -\int_{V_1}^{V_2} PdV \tag{1.20}$$

Note Connecting that to the PV diagram, the work done by the system is the area under the curve in the PV diagram.

Chapter 2

Heat Transfer