Notes on Thermodynamics

The topic for the last part of our physics class this quarter will be thermodynamics. Thermodynamics deals with energy transfer processes. **The key idea is that materials have "internal energy"**. The internal energy is the energy that the atoms and molecules of the material possess. For example, in a gas and liquid the molecules are moving and have kinetic energy. The molecules can also rotate and vibrate, and these motions also contribute to the gases total internal energy. In a solid, the atoms can oscillate about their equilibrium position and also possess energy. The total internal energy is defined as:

The total internal energy of a substance = the sum of the energies of the constituents of the substance.

When two substances come in contact, internal energy from one substance can decrease while the internal energy of the other increases. The first law of thermodynamics states that the energy lost by one substance is gained by the other. That is, that there exists a quantity called energy that is conserved. We will develop this idea and more over the next 4 weeks.

We will be analyzing gases, liquids, and solids, so we need to determine which properties are necessary for an appropriate description of these materials. Although we will be making models about the constituents of these materials, what is usually measured are their **macroscopic quantities** or "large scale" properties of the systems. We have already some of these when we studied fluids in the beginning of the course:

Volume (V): The volume that the material occupies. Volume is a scalar.

Pressure (P): The pressure equals the force/area if a surface is placed in the liquid or gas. Pressure is also a scalar.

Both these quantities are **state variables**. State variables are quantities (macroscopic) that only depend on the state of the system and not on how the system was formed. The systems total internal energy (U) defined above is also a state variable. We will be interested in the relationships between the state variables of a system. One of the most important concepts in thermodynamics is that of temperature. Our first task will be to determine a consistent way to quantify it, that is find a way to measure it and assign a number value to the temperature of a system.

Temperature and Thermometers

We have a general idea of what temperature is: hot things have a higher temperature than colder ones. However, Physics is an exact quantitative science, so we need to be precise with temperature. In order for a system to have a unique temperature it needs to be in thermal equilibrium.

Thermal Equilibrium: A system is in thermal equilibrium if the macroscopic state variables do not change in time.

Before we can assign a number value to the temperature we need to have a qualitative understanding of what temperature is. Temperature is some sort of measure of which way energy will be transfered when two systems are in contact. Energy will flow from a system that has a higher temperature to one that has a lower one. For two systems to have the same temperature, it means that when they are placed in contact there will not be any energy transfer from one to the other. That is, when they are placed in contact with each other, the macroscopic quantities stay the same, i.e. they are in thermal equilibrium. The "Zeroth law" of thermodynamics includes a third system:

Zero'th Law of Thermodynamics: If system A and system B are in thermal equilibrium with system C (i.e. they have the same temperature as C), they they are in thermal equilibrium with each other (i.e. they have the same temperature).

This property of nature enables one to assign a number value to temperature. We just need to choose two reference values, and use a substance with a macroscopic quantity that varies with "our preception of temperature". The substance we call a thermometer.

The Celsius choice of reference values is to assign the triple point of water (where H_2O exists in solid, liquid and vapor forms) to be zero degrees. The other reference value is assigned to be 100 degrees where water and steam co-exist at one atmosphere pressure. Suppose we have a third substance at an unknown temperature T. How do we determine T? One way is to pick a substance to be a thermometer and define T to be proportional to a macroscopic quantity of the substance. Let's demonstrate this with an example.

We will find the value of T of an object using three different substances for thermometers: liquid mercury, a resistor and a dilute gas. As our parameter we will choose the volume of mercury, the resistance of the resistor and the pressure of the dilute gas. Here is our (made-up) data:

Temperature	Height of Hg	Resistance	Pressure of Dilute Gas
100	8.0 cm	3.40 mV	1.37×10^5 Pa
T	6.5 cm	3.24 mV	1.23×10^5 Pa
0	4.0 cm	3.00 mV	1.00×10^5 Pa

The "unknown" temperature T of the object is determined for each thermometer by having the temperature be proportional to the parameter that is changing. So using the mercury thermometer,

$$T = 100(\frac{6.5 - 4.0}{8.0 - 4.0}) = 62.5^\circ \tag{1}$$

Using the resistance thermometer,

$$T = 100(\frac{3.24 - 3.0}{3.4 - 3.0}) = 60.0^\circ \tag{2}$$

Using the dilute gas thermometer,

$$T = 100(\frac{1.23 - 1.0}{1.37 - 1.0}) = 62.2^\circ \tag{3}$$

The data was "made-up", however if real data were used the results would be similar: in general the temperature T can depend on the type of thermometer used. This is because temperature is defined to make the parameter of the thermometer proportional to T. All thermometers will agree at the two reference temperatures. However, in general, the parameters for each thermometer do not have exactly the same behavior between the reference points.

You might ask, which substance is the best to use as a thermometer? Is it possible to define temperature such that the equations of thermodynamics have a simple form for all substances? It would be nice if there were a class of substances that all give the same value for T. There is. After trying different types of thermometers we would discover the following property about the dilute gas thermometer above: we get the same value for T for any gas that we use! That is, if we use air, or H_2, or O_2, or He, etc. the value of T for our object, obtained by measuring the pressure of the gas, would be the same in each case. There are many proerties that all dilute gases have in common. Thus, if we quantify temperature using the constant volume dilute gas thermometer, there is a good chance that this method gives a useful definition of temperature. This will be our first way to quantify temperature.

You might be thinking: How small should the density of the gas be for it to be delute enough? The common properties converge only in the limit as the density of the gas goes to zero. We define an **ideal gas**:

Ideal Gas: The limit as the density of the gas approaches zero of a dilute gas.

We will call the thermometer a constant volume "ideal gas thermometer", and the parameter is the pressure of the gas. Using the references of the Celsius scale, we find that the pressure of the gas would be zero at around $-273°$C. It will be useful to choose the value of temperature when the pressure of an ideal gas is zero to be zero degrees. With this choice we have:

$$T \propto P \tag{4}$$

So temperature is defined to be proportional to the pressure of an ideal gas. The constant of proportionality is chosen such that the change of one degree is the same as the change of one degree Celsius. That is, the difference in temperature between boiling water and the triple point is 100°. For this choice, the proportionality constant becomes 273.16° at the triple point of water.

$$T \equiv \frac{P}{P_{tp}} 273.16 \tag{5}$$

where P_{tp} is the pressure of the gas at the triple point of water. It is important to note that **both pressures must be measured at the same volume of the gas** (Constant Volume Thermometer). The unit of this definition of temperature is the Kelvin (K). To measure temperature in the lab or in our homes we can't carry around a dilute gas and water at the triple point. Commercial thermometer are calibrated against this standard thermometer and have a range of validity.

Are the units of temperature derivable from other fundamental units such as length, time, mass, ...? Or is temperature a fundamental physical quantity? Later in the course we will consider these questions and discuss better ways to define temperature that do not require a thermometer substance at all. One way uses a "Carnot cycle" and the other way is a statistical approach developed by Boltzmann. However, the ideal gas thermometer gives the same value for T as these other approaches. Until we develop the physics behind these other approaches, we will define temperature via the ideal-gas constant-volume thermometer.

Thermal Expansion

When the internal energy of a substance increases, the atoms and molecules gain energy, tend to vibrate with larger amplitudes and the substance usually increases in size. In addition to increasing in size, an increase in internal energy usually is accompanied by an increase in temperature. To a good approximation the fractional increase in size is proportional to the change in temperature.

Consider first a long rod made of a solid material. As long as the change in temperature, ΔT, is not too large, the fractional change in length is proportional to ΔT:

$$\frac{\Delta L}{L_0} \textit{ is proportional to } \Delta T \tag{6}$$

where L_0 is the original length before the increase in temperature. The proportionality constant for **linear expansion** is usually called α:

$$\frac{\Delta L}{L_0} = \alpha \Delta T \tag{7}$$

where α depends on the type of material. If we call L the final length of the rod after the increase in temperature, we have:

$$\frac{L - L_0}{L_0} = \alpha \Delta T \tag{8}$$

or

$$L = L_0(1 + \alpha \Delta T) \tag{9}$$

A rectangular object will expand in the same fractional way. If the original sides of the rectangle are a_0 and b_0, then after a temperature increase of ΔT, side a will increase to $a_0(1 + \alpha\Delta T)$ and side b will increase to $b_0(1 + \alpha\Delta T)$. The new area A will be:

$$A = ab = a_0(1 + \alpha \Delta T) b_0(1 + \alpha \Delta T) \tag{10}$$

multiplying out the terms gives

$$A = a_0 b_0 (1 + 2\alpha \Delta T + (\alpha \Delta T)^2) \tag{11}$$

Since $\alpha\Delta T$ is small, the last term is on the right is much smaller than the middle term, so to a good approximation we have:

$$A \approx a_0 b_0 (1 + 2\alpha \Delta T) \tag{12}$$

Since the original area $A_0 = a_0 b_0$, the equation for "area" expansion is

$$A \approx A_0(1 + 2\alpha\Delta T) \tag{13}$$

Using similar reasoning, one obtains the **volume expansion** formula

$$V \approx V_0(1 + 3\alpha\Delta T) \tag{14}$$

These formulas are not fundamental laws of nature, but rather empirical results and have a limited range of validity. If the temperature keeps increasing, the solid does not keep getting bigger and bigger, but eventually melts.

Energy Transfer Processes

The study of energy transfer processes assumes that all "systems" possess "internal energy". By internal energy we mean the sum of the kinetic and potential energies of the consitituents of the "system". In this course we will consider systems that are bulk materials like gases, liquids, and solids. One can extend these ideas to smaller systems like molecules, atoms or nuclei. Exeriments verify that objects are made up of atoms and molecules and contain internal energy.

The constituents of a system can gain energy or lose energy, and consequently the total interal energy of a system can change. U is denoted as the total internal energy, and

ΔU is defined as the change in the total internal energy of a system

U can change in different ways, but we divide the possibilities into two catagories: those due to mechanical work and those only due a temperature difference:

W is defined as the mechanical work done by a substance

Note the preposition **by** in the defination of W. **If W is positive then the system loses internal energy**, since the system is doing work. **If W is negative then the system gains internal energy**, since work is done on the system. This is the convention chosen by scientists. It will make sense when we use a $P - V$ diagram.

Q is defined as the energy tranfered to the system by processes that don't involve mechanical work

Note that Q is the energy transfered **to** the system, so if Q is positive then so is ΔU. Q is also defined as energy that is transfered as a result of a temperature difference only. Q is also called heat. Heat is a transfer of energy.

Both W and Q have units of energy. The metric unit of energy is the Joule. However, experiments with heat processes were done before it was realized that heat processes could be related to mechanical energy. The unit of the Calorie was used. The conversion from calorie to the Joule, the mechanical equivalent of heat, is 4.186 Joules = 1 calorie. The "calorie" listed on food packages is equal to 1000 calories or 4186 Joules.

In general both types of processes can occur at the same time, so the change in U is the sum of these two energy transfer processes:

$$\Delta U = Q - W \tag{15}$$

The minus sign on W is due to the definition of W as the work done by the system. This equation is called **the first law of thermodynamics**. It is a statement recognizing the existence of internal energy and its conservation.

Some Heat Processes

When a system gains (or loses) internal energy, the temperature of the system usually changes. It is interesting to measure how much the temperature changes for a certain amount of internal energy change. Here we consider how much the temperature changes due to heat processes.

Suppose we have a particular substance, whose mass is m. If we transfer an amount of energy Q into the substance, keeping its volume constant, the temperature of the substance will in general change. Call the change in temperature ΔT. How is Q related to m and ΔT? If m is doubled, we will need twice the amount of energy transfered ($2Q$). This is true, since doubling the mass is the same has having two identical samples. Twice the energy is needed. So for the same ΔT, $Q \propto m$. Also, if ΔT is not too large, if we want twice the temperature change, we will need twice the energy transfer. So for a fixed mass, $Q \propto \Delta T$. Combining these two proportions gives:

$$Q \propto m\Delta T \tag{16}$$

We can make this an equal sign by adding a constant of proportionality:

$$Q = c_v m\Delta T \tag{17}$$

The parameter c_v is called the **specific heat capacity** for the process in which the volume is held constant. Note that this is not a new fundamental law of nature, but rather a phenomenological equation. c_v will depend on the type of substance and can also depend on temperature. If ΔT is so large that c_v changes with T, then one has to integrate:

$$Q = \int_{T_i}^{T_f} c_v(T) m \, dT \tag{18}$$

where T_i and T_f are the initial and final temperatures respectively. An important feature of specific heat capacities is that they are measureable quantities. The challenge we have as a physicist is to understand c_v from the microscopic structure of the substance. In this course we will do this for gases.

If the heat capacity of a substance is large, it means that it takes a lot of energy transfer to increase the temperature a little. Likewise, if a substance has a high heat capacity, it has to lose a lot of internal energy for a small temperature change. It stays "hot" for a long time. The cheese on a pizza has a higher heat capacity than the bread crust.

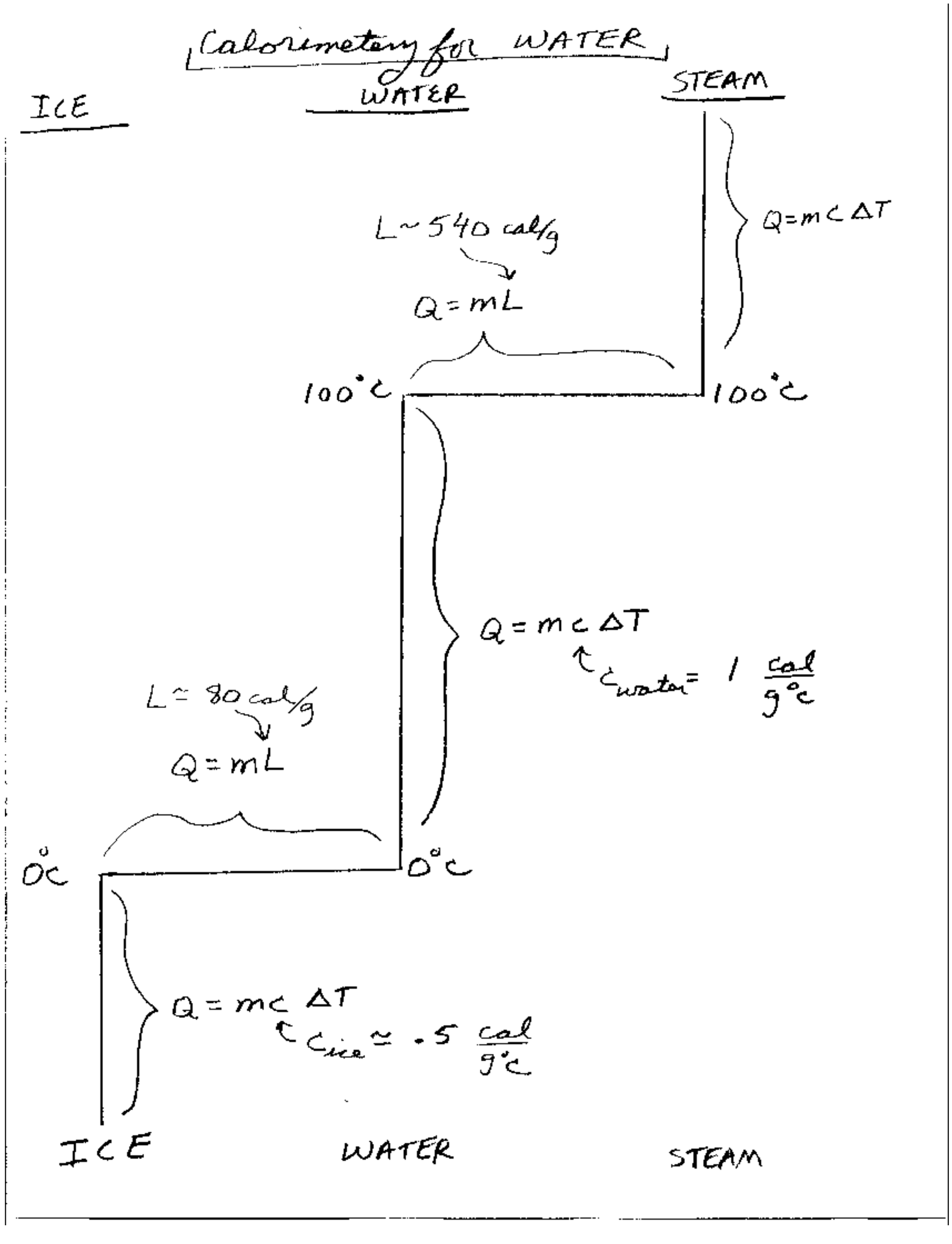
Latent Heat

Latent heat is the amount of energy transfer (per mass) that is needed to change the phase of a substance. For example, if you heat up water on the stove the temperature rises until it reaches 100°C. As more energy is transfered to the water the temperature does not increase any more. Rather, the water evaporates and changes its state from liquid to vapor. The amount of energy transfer that is required for this phase change (per unit mass) is called the latent heat. Tt takes twice the amount of energy to change the phase of twice the mass. So, we have:

$$Q = mL \tag{19}$$

where Q is the amount of energy tranfered (heat) to change the phase of a substance of mass m. The proportionality constant L is called the **latent heat** and has units of Joules/Kg, or cal/g. If the phase change is from solid to liquid (or liquid to solid) L is called the latent heat of fusion. If the phase change is from liquid to vapor (or vapor to liquid) L is called the latent heat of vaporization.

I have included a nice schematic of the energy transfers involved for water at one atmosphere as it gains or loses energy. See the attached figure. The three different states of water go from left to right, and the temperature goes up and down. Similar schematics can be drawn for other substances.


Calorimetry for WATER
ICE
WATER
STEAM
$Q = mc\Delta T$
$L \sim 540$ cal/g
$Q = mL$
100°C
100°C
$Q = mc\Delta T$
$c_{water} = 1 \frac{cal}{g°C}$
$L \simeq 80$ cal/g
$Q = mL$
0°C
0°C
$Q = mc\Delta T$
$c_{ice} \simeq .5 \frac{cal}{g°C}$
ICE
WATER
STEAM

Thermal Conductivity

Before we carry out a microscopic analysis of a dilute gas, we mention one relationship that pertains to (one dimensional) thermal conduction. Consider a rod of length l and area A. Let the left end be in contact with a large object that is at a temperature T_A. Let the right end be in contact with a large object that is at a temperature T_B. What is the rate H at which energy is transfered through the rod? The units of H are energy/time. What does H depend on?

Area: The larger the area A, the faster energy can be transfered, so $H \propto A$.

Length: The longer the length l that the rod is, the slower is the energy transfer, so we will guess that $H \propto 1/l$.

Temperature difference: The larger that $T_A - T_B$ is, the faster the energy will be transfered, so $H \propto (T_A - T_B)$.

Putting these ideas together we have

$$H \propto \frac{(T_A - T_B)A}{l} \tag{20}$$

Changing the proportionality by an equal sign brings in a constant k:

$$H = k\frac{(T_A - T_B)A}{l} \tag{21}$$

where k is called the thermal conductivity.

It is interesting to include both the properties of heat capacity and thermal conductivity in one application. Suppose the object at the left end of the rod has a mass m and a specific heat capacity of c_v. Let the temperature on the right, T_B, be held constant, but let the temperature of the object on the left decrease as it loses energy. Let T be the temperature of the object on the left at time t. Then we have:

$$H = k\frac{(T - T_B)A}{l} \tag{22}$$

where H is the energy loss per second of the left object. The amount of energy, Q, the object loses in a time Δt is

$$Q = H\Delta t = k\frac{(T - T_B)A}{l}\Delta t \tag{23}$$

Since $Q = mc_v \Delta T$, we have

$$mc_v \frac{\Delta T}{\Delta t} = -k \frac{(T - T_B)A}{l} \tag{24}$$

Taking the limit as Δt goes to zero results in a simple differential equation:

$$\frac{dT}{dt} = -k \frac{(T - T_B)A}{mc_v l} \tag{25}$$

Since T_B is a constant, $dT/dt = d(T - T_B)/dt$. If we define the temperature difference between the left and right sides, $(T - T_B)$, as δT, we have:

$$\frac{d(\delta T)}{dt} = -\frac{kA}{mc_v l}(\delta T) \tag{26}$$

This is a simple differential equation whose solution is an exponentially decaying function:

$$\delta T = (\delta T)_0 e^{-\frac{kA}{mc_v l} t} \tag{27}$$

where $(\delta T_0$ is the initial temperature difference between the left and right side. Thus the temperature decreases exponentially to its final value. This type of cooling is called Newton's cooling.

Convection: Energy transfered by a movement of mass is called convection. Some demonstrations of convection will be presented in class, but we will not do a quantitative analysis of convection.

Radiation Energy can also be tranfered through a vacuum (as well as air). Objects naturally "radiate" electro-magnetic energy. The electro-magnetic interaction will be covered next quarter. Here we present the formula, without derivation, of the amount of electro-magnetic energy radiated from an object at a temperature T:

$$P = \sigma A e T^4 \tag{28}$$

where P is the energy/sec (power) radiated, A is the area of the object, e is the emissivity, and T is the temperature in K. σ is a constant, the Stefan-Boltzmann constant and is equal to 5.669×10^{-8} K^4 $\mathrm{W/m}^2$. The emissivity depends on the properties of the object and takes values between zero and one.

Ideal Gases

Experiments on an Ideal Gas

Our discussion so far has been phenominological. That is, we have been finding empirical formulas that relate (and define) certain quantities. Now we would like to do some physics. We would like to understand the relationships between macroscopic quantities from a microscopic model of the substance. In physics we usually start with the simplest systems first, then extend our ideas to more complicated situations. Due to the universality of ideal gases in defining temperature, we suspect that an ideal gas might be a system for which a simple model will explain many properties. For the rest of the course we will mainly analyze ideal gases and see what they can teach us about energy transfer processes.

Let's first summarize the experimental data on ideal gases. Remember an ideal gas is a dilute gas in the limit that the density approaches zero. Think of an ideal gas as a very dilute gas. The main macroscopic measureable quantities that describe an ideal gas are:

Volume (V): the volume of the container that confines the gas.

Pressure (P): The pressure in the gas. If the gas is in equilibrium then the pressure is the same everywhere (neglecting gravity).

Temperature (T): We have used ideal gases to define temperature. If the gas is in equilibrium, the temperature is the same everywhere.

Mass or Number of Molecules (N): The mass of a gas can be measured, and we assume that N, the number of molecules, is proportional to its mass. We will use the parameter N, although difficult to measure, could be determined using Avogadro's number.

How are these four quantities related to each other. We need to keep two fixed and experimentally determine how the other two depend on each other.

N and V held constant
How does T depend on P? We defined temperature to be proportional to P, so

$$T \propto P \tag{29}$$

Although we defined T so this proportionality is true, the fact that we get the same value for T no matter what the gas is something special. It is a nice experimental result.

N and T held constant
How does P depend on V? If the volume of a gas is increases with constant temperature, the pressure is reduced. We will show in lecture that:

$$P \propto \frac{1}{V} \tag{30}$$

This is a really nice and simple experimental result! Why is it so simple? What can we learn from this relationship?

T and V held constant
How does P depend on N? We will show in lecture that:

$$P \propto N \tag{31}$$

We can combine the results of these three experiments into one equation:

$$P \propto \frac{NT}{V} \tag{32}$$

N and P held constant
How does V depend on T in this case? From the above equation we must have $V \propto T$, which is verified experimentally.

We can replace the proportionality sign with an equal sign by adding a proportionality constant:

$$P = \frac{NkT}{V} \tag{33}$$

where the constant k is called Boltzmann's constant. We will discuss its value later. This equation is also written in terms of the number of moles of the gas by multiplying and dividing by Avogadro's number, N_A:

$$\begin{aligned} Nk &= (\frac{N}{N_A})(N_A k) \\ &= nR \end{aligned}$$

where n is the number of moles of the gas, and R is called the gas constant. Note that $R = N_A k$. The **equation of state for an ideal gas** is often written as:

$$PV = nRT \tag{34}$$

The constant R is measureable, once we have decided on how much mass a mole is and our temperature scale (i.e. ΔT between boiling water and the triple point). We need to measure the pressure, volume and Temperature for a known number of moles. The resuls is:

$$R \approx 8.34 \frac{Joules}{mole\,^\circ K} \tag{35}$$

Once Avagadro's number is known to be 6.02×10^{23} then $k = 1.38 \times 10^{-23}\ J/^\circ K$.

Our task now is to come up with a microscopic model to explain this equation of state. There are other experimental quantites to compare with, c_v being one of them. First, we will try to understand the equation of state.

Kinetic Theory: A model for ideal gases

Consider a dilute gas that is contained in a box with sides of equal length L. Our model of a gas is that it consists of a large number N of molecules that are "bouncing around" inside the container. We will assume that the molecules bounce off each other and the sides of the container elastically. That is, the molecules do not lose kinetic energy in the collisions. We will also neglect the gravitational potential energy of the molecules, mgy. This will be OK if the kinetic energy of each molecule is much larger than mgL. As we will see, this is a good approximation.

Pressure is force/area. How are the molecules applying a force to the sides? By bouncing off, their momentum is changed. Force is change in momentum per time. Let's determine the change in momentum of a molecule as it bounces off a side of the box, a side in the y-z plane.

1. **Momentum Change per bounce**: Momentum is $m\vec{v}$. When a molecule bounces *elastically* off a side (in the y-z plane), the x-component of its velocity gets reversed. The x-component of its momentum changes from mv_x to $-mv_x$. This is a *net change* of

$$2mv_x$$

2. **Force of one molecule on side**: The force the side feels from this one molecule will be: (the number of times the molecule hits the side per second) times $2mv_x$, since force is (momentum change)/time. The number of times the molecule hits the side

per second is $v_x/(2L)$. So the force of one molecule on the side is: $(2mv_x)(v_x/(2L)$ or

$$mv_x^2/L$$

3. **Average Pressure one molecule exerts on one side**: Since pressure is force/area, the pressure is just $(mv_x^2/L)/L^2$ or mv_x^2/L^3. As the molecules bounce off each other they will have collisions at different angles and their speeds will change. At any time the speeds of the molecules in a gas will have a range of values. To find the average pressure, we should take the average value of v_x^2 which we write as $\overline{v_x^2}$. So the average pressure that one molecule exerts on a side (in the y-z plane) is

$$\frac{m\overline{v_x^2}}{L^3} \tag{36}$$

4. **Average Pressure for N molecules**: If there are N molecules in the gas, then the average pressure on a side is:

$$P = \frac{Nm\overline{v_x^2}}{L^3} \tag{37}$$

Similarly, the average pressure on a side in the x-y plane is $P = Nm\overline{v_z^2}/L^3$ and on a side in the x-z plane is $P = Nm\overline{v_y^2}/L^3$. If a molecule is equally likely to move in any direction, then $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$. Since the magnitude of the velocity is $v^2 = v_x^2 + v_y^2 + v_z^2$, we have $\overline{v_x^2} = \overline{v^2}/3$. Substituting this into the equation above we have:

$$P = \frac{Nm\overline{v^2}}{3L^3} \tag{38}$$

However, $V = L^3$, so the equation can be written

$$P = \frac{N}{V}(\frac{m\overline{v^2}}{3}) \tag{39}$$

Wow, the model is consistent with the data. The equation states that pressure is proportional to N and inversely proportional to V as demonstrated by experiment. The terms on the right side deserve some comment.

Why $1/L^3$? Pressure is Force/Area, and Area goes as L^2. The other factor of L in the denominator is because the larger L is, the molecules will have fewer collisions/sec with the sides. Hence, the pressure is proportional to $1/L^2$ times $1/L$.

Why $\bar{v^2}$?: One power of v is because momentum is proportional to velocity. The other power of v is because the faster the molecule travels the more often it will hit the side. Hence, pressure is proportional to the average of v^2.

Why N? The pressure is proportional to N because the number of collisions with the wall per sec is proportional to the number of molecules in the container.

In addition to understanding the data, the above equation gives us an expression relating temperature and the average kinetic energy of a molecule in the gas. The Kinetic Theory gives $(PV/N) = m\bar{v^2}/3$, and experiment yields $(PV/N) = kT$. Equating the right sides of these equations gives:

$$kT = \frac{m\bar{v^2}}{3} \tag{40}$$

Remembering that the kinetic energy equals $mv^2/2$, we can write the right side in terms of the average kinetic energy of a gas molecule:

$$kT = \frac{2}{3}\,\overline{K.E.} \tag{41}$$

where $\overline{K.E}$ is the average kinetic energy of a molecule in the gas.

Temperature Revisited: The temperature T used in these equations was defined using an ideal-gas constant-volume thermometer. The kinetic theory model gives $PV = (2/3)N\overline{K.E.}$. Thus, if V is held constant then P is proportional to the average kinetic energy of a molecule. The constant volume thermometer defines T proportional to P. So, using an ideal-gas constant-volume thermometer is essentially defining temperature to be proportional to the average $K.E.$ per molecule. With this definition of T, it doesn't matter which type of gas is used. This explains the universal nature of an ideal-gas thermometer.
Note: For the ideal gas, it is OK to think of temperature as the average kinetic energy per molecule. However, this is not true in general. We will discuss a broader concept of temperature later. Nonetheless, kT has units of energy, and temperature does not require a new unit. It can always be coupled with k and hence the units of energy.

R.M.S. Velocity: From our model, we can calculate the average speed of a gas molecule. The easiest "speed" to calculate is the root-mean-square speed or RMS speed. The RMS speed is the square-root of the average speed-squared: $v_{rms} \equiv \sqrt{\bar{v^2}}$. From our equation above,

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} \tag{42}$$

where M is the *molar mass* of the gas. Remember **T must be in Kelvin**. Let's calculate v_{rms} for N_2 at room temperature of $T = 293°$K. $v_{rms} = \sqrt{3(8.34)293/(0.028\ kg)} \approx$ 510m/s. The air molecules are hitting you with an average speed of 510m/s. Our assumption that the kinetic energy is much greater than mgL is OK.

Internal Energy of an Ideal Gas

From the kinetic theory model we can obtain an expression for the total internal energy U of an ideal gas. The simplest form would be the sum of the kinetic energies of the molecules. If the gas contains N molecules:

$$U = N\frac{m\bar{v^2}}{2} \tag{43}$$

Using $m\bar{v^2} = 3kT$, U can be expressed in terms of N and T:

$$U = \frac{3}{2}NkT = \frac{3}{2}nRT \tag{44}$$

This is result is due to our definition of T and the properties of an ideal gas. If the number of molecules are fixed, the total energy U only depends on the temperature T. Another way of writing the equation is to use P and V. Since $NkT = PV$, we have $U = (3/2)PV$. However, it is nicer to recognize that U depends on only one parameter T.

Heat Capacity of an Ideal Gas at Constant Volume: Heat capacity relates the temperature increase to the energy transfered to the substance. For gases it is convenient to consider the **heat capacity per mole** of the gas. If the volume is held fixed during the process, no work is done by the gas, so $Q = \Delta U$, so we have

$$Q = \Delta U = \frac{3}{2}nR\Delta T \tag{45}$$

So, $c_v = (3/2)R = 12.5$ Joules/°C per mole of the gas. The measured values of c_v for the nobel gases (e.g. He, Ne, A, and Kr) are very close to this value for all temperatures where the elements are gases. The measured values of c_v per mole for other gases are also close to 12.5 Joules/°C *for low temperatures.*

Since the kinetic theory explains many properties of gases, we are now ready to examine some thermodynamic processes for ideal gases. We first consider monatomic gases, since they are the simplest.

Processes for a Monatomic Ideal Gas

By a "process" we mean that some of the parameters of a gas (V, P, and/or T) are varied as the gas changes from one state to another. For most of the processes we consider, N will not change. Many kinds of processes are possible. Here we will consider some simple ones. We will mainly analyze processes that are "reversible" or equivalently "quasi-static":

Reversible Processes: A slow or "quasi-static" process in which the system is always in equilibrium.

In a process, the internal energy U can change. This change is due to work done **by** the gas W, and energy transfered due to temperature differences Q. Processes can be graphically represented by a plot in the $P-V$ plane. The pressure P is plotted on the vertical axis, and the volume V is plotted on the horizontal axis. The work done by the gas is easily determined in the $P-V$ plane.

Work done by a gas

Work is force times displacement. The work done **by** a gas is the force it exerts times the distance the force acts. However, force is pressure times area. Thus, the work done by the gas is the pressure P times area times the distance the area moves. Area times distance is the change in the volume of the gas, ΔV. So if the volume of a gas changes by an amount ΔV, the gas does work W equal to $P\Delta V$:

$$W_{by\,gas} = P\Delta V \tag{46}$$

If the pressure changes as the volume changes, then one needs to integrate PdV:

$$W_{by} = \int PdV \tag{47}$$

In the $P-V$ plane, **the work is just the area under the curve** representing the process. Using this equation for W_{by}, and the relationship $\Delta U = (3/2)nR\Delta T$, we can determine these two quantites and Q for any process involving ideal monatomic gases.

Isometric Process: An isometric process is a process in which the **volume is constant**, $\Delta V = 0$. P and T will change. In this case, $W = 0$. $Q = \Delta U = (3/2)nR\Delta T$. If the initial pressure is P_i and the final pressure is P_f, $Q = (3/2)nR(T_f - T_i) = (3/2)(P_f V - P_i V)$. So $Q = (3/2)V(P_f - P_i)$. The chart below summarizes our results:

W_{by}	Q	ΔU
0	$\frac{3}{2}nR\Delta T$ or $\frac{3}{2}V(P_f - P_i)$	$\frac{3}{2}nR\Delta T$

Isobaric Process: An isobaric process is one in which the **pressure is held constant**. V and T will change. So the work done by the gas is: $W_{by} = P\Delta V$, or $W_{by} = P(V_f - V_i)$. Since $PV = nRT$, the work done by the gas can also be written in terms of the initial and final temperatures: $W_{by} = nR(T_f - T_i) = nR\Delta T$ for the isobaric process. The change in internal energy ΔU is determined by the change in temperature, so $\Delta U = (3/2)nR\Delta T$. Q for the isobaric process can be determined from:

$$\Delta U = Q - W_{by} \tag{48}$$

or

$$\begin{aligned} Q &= \Delta U + W_{by} \\ &= \frac{3}{2}nR\Delta T + nR\Delta T \\ Q &= \frac{5}{2}nR\Delta T \end{aligned}$$

The factor $(5/2)nR$ is a **heat capacity for a constant pressure process**. The heat capacity at constant pressure per mole of a monatomic gas is $c_p = (5/2)R = 20.8$J/°K. Note: $c_p > c_v$. It takes more heat to raise the temperature for an isobaric process than an isometric process. This is because in an isobaric process some energy is used by the gas as it does work expanding. The experimental data for c_p agree well with this value for the nobel gases at all temperatures.

W_{by}	Q	ΔU
$P(V_f - V_i)$ or $nR\Delta T$	$\frac{5}{2}nR\Delta T$	$\frac{3}{2}nR\Delta T$

Isothermal Process: An isothermal process is one in which the **temperature is held constant**. P and V will change. Since U is proportional to T, if $\Delta T = 0$ then $\Delta U = 0$. This means that

$$Q = W_{by} \tag{49}$$

Consider an isothermal process in which the volume increases from V_i to V_f. From the ideal gas law: $P = nRT/V$, so the pressure decreases as V increases if T is constant. Since the pressure changes, to find the work done by the gas, we need to integrate:

$$W_{by} = \int_{V_i}^{V_f} P dV \tag{50}$$

Since $P = nRT/V$ during the isothermal volume expansion,

$$W_{by} = \int_{V_i}^{V_f} \frac{nRT}{V} dV \tag{51}$$

the nRT factors out of the integral and we have

$$W_{by} = nRT \int_{V_i}^{V_f} \frac{dV}{V} \tag{52}$$

The integral is easily solved to give

$$W_{by} = nRT ln(\frac{V_f}{V_i}) \tag{53}$$

and so $Q = W_{by} = nRTln(V_f/V_i)$.

W_{by}	Q	ΔU
$nRT\ ln(V_f/V_i)$	$nRT\ ln(V_f/V_i)$	0

Adiabatic Process: An adiabatic process is one in which $Q = 0$. In this case, $\Delta U = -W_{by}$. Suppose a gas starts out with a initial volume V_i and pressure P_i. If the volume is then increased slowly to a value $V > V_i$, what is the pressure? Since the temperature will change in this process, P does not equal $V_i P_i / V$. That is, although $PV = nRT$ at any moment of the process, T is changing and so is the product PV. To determine how P changes with V, we start with:

$$\Delta U = -W_{by} = -P\Delta V \tag{54}$$

Since $U = (3/2)nRT = (3/2)PV$ for a monatomic gas, we have

$$\frac{3}{2}\Delta(PV) = -P\Delta V \tag{55}$$

Using the product rule for differentials

$$\frac{3}{2}(P\Delta V + V\Delta P) = -P\Delta V \tag{56}$$

Rearrainging terms:

$$\frac{3}{2}\frac{\Delta P}{P} = -\frac{5}{2}\frac{\Delta V}{V} \tag{57}$$

Taking the limit at $\Delta P \to 0$ and $\Delta V \to 0$ gives

$$\frac{3}{2}\int \frac{dP}{P} = -\frac{5}{2}\int \frac{dV}{V} \tag{58}$$

After integrating, the equation becomes

$$\frac{3}{2}lnP + \frac{5}{2}lnV = ln(P^{3/2}V^{5/2}) = Const \tag{59}$$

If we define the parameter $\gamma \equiv 5/3$, then during the adiabatic process

$$PV^{\gamma} = P_i V_i^{\gamma} \tag{60}$$

The work is found by integrating $\int PdV$:

$$W_{by} = \int_{V_i}^{V_f} \frac{P_i V_i^{\gamma}}{V^{\gamma}} dV \tag{61}$$

which, after some algebra, is

$$W_{by} = \frac{P_i V_i}{\gamma - 1}(1 - (\frac{V_i}{V_f})^{\gamma-1}) \tag{62}$$

This work done by the gas will decrease the internal energy. It is interesting to calculate the change in temperature in adiabatic process. Since $PV^{\gamma} = const$,

$$P_i V_i^{\gamma} = P_f V_f^{\gamma} \tag{63}$$

Using $P = (nRT)/V$ we have

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \tag{64}$$

or

$$T_f = T_i(\frac{V_i}{V_F})^{\gamma-1} \tag{65}$$

For a monatomic gas, $\gamma = 5/3$, so $\gamma - 1 = 2/3$. If the volume decreases by a factor of 2, then the final temperature in Kelvin increases by a factor of $2^{2/3} = 1.59$. A volume change by 5 gives $5^{2/3} = 2.92$, and a ten-fold change gives $10^{2/3} = 4.64$. The work done "on" the gas increases the internal energy. That *the temperature is correctly predicted by our model supports the hypothesis* of the first law of thermodynamics: that *mechanical work can be directly converted into internal energy.*

Closed Cycle Processes

By a closed cycle process we mean a process which ends at the same state that it started. If the final state is the same as the initial state, then $U_f = U_i$ and $\Delta U = 0$ for the closed cycle. However, the work done in the closed cycle will not be zero, but rather the area enclosed by the process in the $P - V$ plane. We will demonstrate these ideas with an example, which uses specific values for the states.

Our system will be **2 moles of** He, which is a monatomic gas.

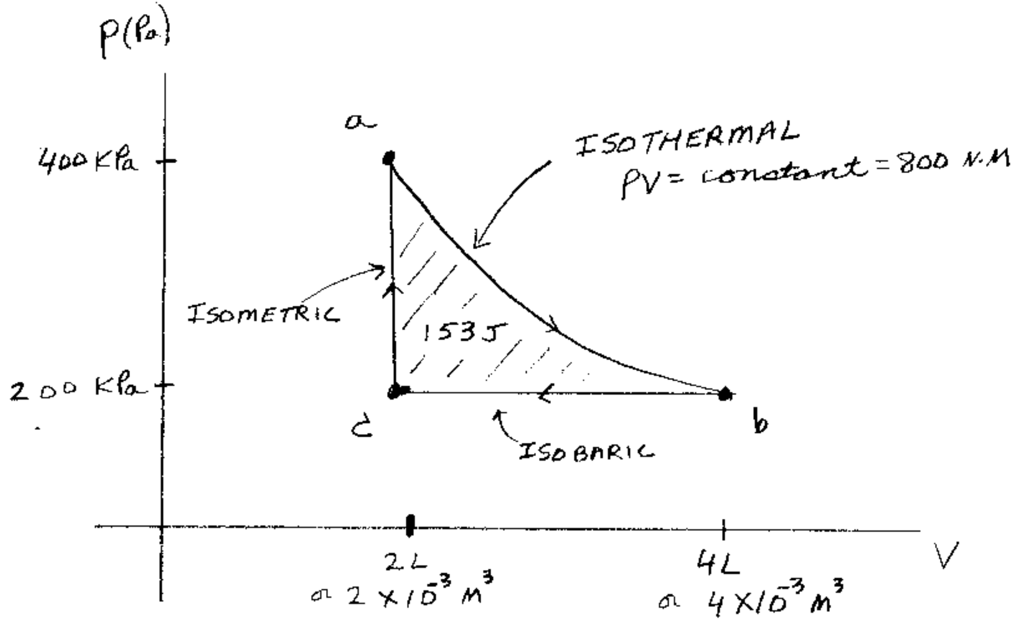
State a: Volume = 2 liters; Pressure = 400×10^3Pa.
State b: Volume = 4 liters; Pressure = 200×10^3Pa.
State c: Volume = 2 liters; Pressure = 200×10^3Pa.

Note: With this information, we can calculate the temperatures of the different states. Since $T = (PV)/(nR)$, we have $T_a = (400 \times 10^3)(2 \times 10^{-3})/((2)(8.314)) = 48$°K. Here we have used the conversion 1 *liter* $= 10^{-3} m^3$. Similarily, $T_b = 48$°K and $T_c = 24$°K. The gas changes from state $a \rightarrow b \rightarrow c \rightarrow a$. We will calculate ΔU, Q, and W_{by} for each leg of the process. The results are:

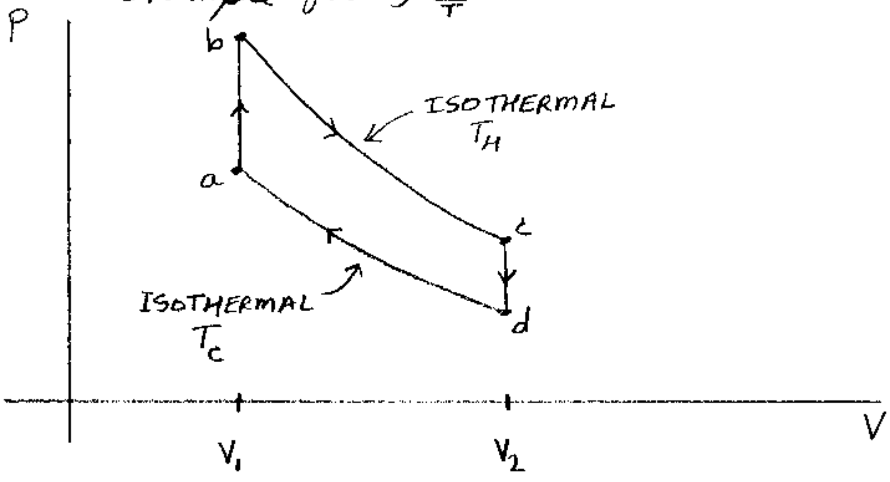
Process	W_{by} (Joules)	Q (Joules)	ΔU (Joules)
$a \rightarrow b$ (isothermal)	553	553	0
$b \rightarrow c$ (isobaric)	-400	-998	-598
$c \rightarrow a$ (isometric)	0	598	598
Whole Cycle	153	153	0

We could repeat this cycle over and over again. What is happening per cycle? 153 Joules of energy is added to the system, and the system does 153 Joules of work.

Example for 2 moles of He



Example for $\oint \frac{dQ}{T}$



This is what an engine is supposed to do. A closed clockwise cycle will function as an engine. A closed counter-clockwise cycle will function as a refrigerator. For our engine cycle, a net $Q_{in} = 553 + 598 = 1151$ Joules is transfered into the gas, and a net $Q_{out} = 998$ Joules is transfered out of the gas. The difference $W_{by} = Q_{in} - Q_{out}$ is the work done by the gas.

What we would like to have happen is for most of the Q_{in} to be converted to work, and little transfered out: Q_{out}. We define the **efficiency**, ϵ, of a "heat-engine" to be:

$$\epsilon \equiv \frac{W_{by}}{Q_{in}} \tag{66}$$

This equation can also be written as

$$\epsilon \equiv 1 - \frac{Q_{out}}{Q_{in}} \tag{67}$$

since $W_{by} = Q_{in} - Q_{out}$. For our example, $\epsilon = 153/1151 \approx 0.13$, or a 13% efficiency. How can we make the efficiency large? What kind of cycle is the best? The answers to these important engineering questions require some thought and lead to some new ideas: the second law of thermodynamics and entropy. We will tackle these problems for the monatomic ideal gas, since we have a nice working model and it is a simple system. Then we will generalize our results.

Entropy

When ΔU was summed up for a closed cycle the net change was zero. This is because U is a state function of the system. It only depends on the state itself, and not how the state was formed. We represent the sum of ΔU for a closed cycle as the integral $\oint dU$. Since U is a state function $\oint dU = 0$. Examples of other state functions are V, P, and T. Q and W are not state functions. $\oint dQ$ is not zero as demonstrated by our last example. $\oint dW = \oint p dV$ is also not equal to zero in general, but is the area enclosed by the path of the cyclic process.

We would like to have a state function involving dQ. Equivantly, we need to find an expression with dQ such that when integrated over a complete cycle gives zero. Then we will have something absolute about Q, which will help us determine the maximum energy efficiency. We shall show that $\oint dQ/T$ is zero for any closed cycle for an ideal gas. First we will do a specific closed cycle example and calculate $\int dQ/T$ to show that $\oint dQ/T = 0$. Then we will prove it for the general case of an ideal gas.

Consider a closed cycle process for an ideal monatomic gas that is bounded by two isothermal processes and two isometric processes. We will calculate the following table in lecture for the 4 legs:

Process	W	Q	ΔU	$\int dQ/T$
$a \to b$	0	$(3/2)nR(T_H - T_C)$	$(3/2)nR(T_H - T_C)$	$(3/2)nR\ ln(T_H/T_C)$
$b \to c$	$nRT_H\ ln(V_2/V_1)$	$nRT_H\ ln(V_2/V_1)$	0	$nR\ ln(V_2/V_1)$
$c \to d$	0	$-(3/2)nR(T_H - T_C)$	$-(3/2)nR(T_H - T_C)$	$(3/2)nR\ ln(T_C/T_H)$
$d \to a$	$nRT_C\ ln(V_1/V_2)$	$nRT_C\ ln(V_1/V_2)$	0	$nR\ ln(V_1/V_2)$
cycle	$nR(T_H - T_C)$ $ln(V_2/V_1)$	$nR(T_H - T_C)$ $ln(V_2/V_1)$	0	0

where $a \to b$ and $c \to d$ are isometric (constant V) processes, and $b \to c$ and $d \to a$ are isothermal (constant T) processes.

Note that $\oint dQ/T = 0$ for any value of V_1, V_2, T_H, or T_C. Is this true for any closed cycle? The answer is yes. We can prove it for a monatomic ideal gas:

$$0 = \oint \frac{dV}{V} \tag{68}$$

For any closed cycle, the above integral is just $lnV_i/V_i = ln(1) = 0$. Using the equation for an ideal gas,

$$0 = \oint \frac{pdV}{nRT} \tag{69}$$

However, pdV equals $dQ - dU$ from the first law of thermodynamics.

$$0 = \oint \frac{dQ - dU}{nRT} \tag{70}$$

For a monatomic gas, $U = (3/2)nRT$. With this substitution we have

$$0 = \oint \frac{dQ}{nRT} - \frac{2}{3} \oint \frac{dU}{U} \tag{71}$$

The second integral is zero, since $\oint dU/U = ln(U_i/U_i) = ln(1) = 0$. Canceling out the nR

$$0 = \oint \frac{dQ}{T} \tag{72}$$

Although this derivation was for the monatomic gas, the same line of reasoning will work for any ideal gas. The only difference in the derivation will be that $U = f(T)$, that is U is only a function of T. This is the key property of the system. If U only depends on T, $U(T)$, then then the integral of $\int dU/T = \int (U'(T)/T)dT$, where

$U'(T) = dU/dT$. This integral will be zero over a closed cycle, since the integrand only depends on T.

The above result has profound consequences. It means that if $\Delta Q/T$ is summed up from one state a to another state b, the integral $\int_a^b dQ/T$ is the same for any process that changes the system from $a \to b$. The quantity $\int_a^b dQ/T$ only depends on the initial state a and final state b. This integral we call the **entropy difference** between the two states. Entropy is given the symbol S:

$$S(b) - S(a) = \int_a^b \frac{dQ}{T} \tag{73}$$

Entropy is a "state function" of a system, just like U, V, T, and P. Before we try and identify what S depends on for a gas, we should remind ourselves on how it was discovered using a thermodynamics approach. The important step in making $\oint dQ/T = 0$, was $\oint dU/T = 0$. This was made possible by our definition of temperature, which ended up being (for an ideal gas) proportional to the average kinetic energy per molecule and hence proportional to U. We can turn the argument around, and say that **it is possible to define temperature T such that $\oint dQ/T = 0$ for any cyclic process**. This definition of temperature is independent of any thermometer, and this statement recognizes the existance of the entropy state function.

Other Topics

Diatomic and other ideal gases

For all gases, the equation of state $PV = nRT$ is valid in the limit of an ideal gas (i.e. in the limit as the density goes to zero). The next most complicated gas after a monatomic gas is a diatomic gas, whose molecule has two atoms, e.g. H_2, O_2, N_2. The energy U for n moles of a monatomic gas was found to be $(3/2)nRT$. We can determine how the energy of a diatomic gas depends on temperature by measuring the heat capacity (per mole) for a constant volume process.

In a constant volume process, $\Delta U = Q = c_v \Delta T$. A graph of c_v for H_2 as a function of temperature will be shown in lecture. At low temperatures, $c_v = (3/2)R$ which is the same as the monatomic gas. However, as the temperature increases, c_v jumps up to $(5/2)R$ at around 150°K. After a further increase in T, c_v jumps up to $(7/2)R$ at around 3000°K. This behaviour is strange for two reasons: 1) the sudden increase (or jump) of c_v as a function of T, and 2) the first increase from $(3/2)R$ to $(5/2)R$. The understanding of these features required "new" physics, quantum mechanics, which we cover in our modern physics course (Phy235).

Qualitatively, we understand the sudden increase in U for a diatomic molecule as rotational energy and vibrational energy. A diatomic molecule can translate (like a monatomic gas) in 3 different directions, rotate in 3 different directions and vibrate (two degrees of freedom). There is a theorum, **the equipartition theorum**, which states that for every degree of freedom that contributes quadratically to the energy, the average energy is $(RT)/2$ per mole. If only translation is allowed, $U = (3/2)RT$, since there are three directions, each of which contribute $(RT)/2$. Rotations should add $3 \times (1/2)RT = (3/2)RT$, but they only seem to add RT to the energy/mole. These descrepancies are resolved using quantum mechanics.

For our applications here, we just need to know c_v for the conditions of our gas. Then,

$$\Delta U = nc_v\Delta T \tag{74}$$

At room temperature, 300°K, N_2, O_2 and H_2 have $c_v = (5/2)R$. The heat capacity at constant pressure is found in terms of c_v as:

$$c_p = c_v + R \tag{75}$$

This can be shown as follows:

$$\begin{aligned} \Delta U &= Q - p\Delta V \\ nc_v\Delta T &= Q - p\Delta V \end{aligned}$$

Now for a constant pressure process, $p\Delta V = \Delta(pV)$. So we have

$$\begin{aligned} nc_v\Delta T &= Q - \Delta(pV) \\ &= Q - \Delta(nRT) \\ n(c_v + R)\Delta T &= Q \end{aligned}$$

which gives $c_p = c_v + R$.

The main difference between ideal gases and ideal monatomic gases (in our treatment) is that c_v and hence c_p depend on energy and might be different than the monatomic values of $(3/2)R$ and $(5/2)R$ respectively. This results in γ being different also, since $\gamma \equiv c_p/c_v$.

Efficiency and the Carnot Cycle

Using $\oint dQ/T = 0$, we can determine an upper limit for efficiency of an engine. Consider a closed cycle (for an ideal gas) that acts like an engine. That is, the path is clockwise in the $P - V$ plane. Divide the path into small segments. For each segment, energy will either enter the system as heat ($\Delta Q(in)$ or leave the system as heat $\Delta Q(out)$. ΔQ could also be zero. Label the segments for which energy enters as i, and those for which energy leaves as j, where both i and j are summed. From $\oint dQ/T = 0$ we have:

$$\sum_i \frac{Q_i(in)}{T_i} - \sum_j \frac{Q_j(out)}{T_j} = 0 \tag{76}$$

where we have taken $Q_j(out)$ to be the absolute value of $Q_j(out)$. The equation can be re-written

$$\sum_i \frac{Q_i(in)}{T_i} = \sum_j \frac{Q_j(out)}{T_j} \tag{77}$$

Let $T_{hottest}$ be the largest value of the temperature during the cycle, and let $T_{coldest}$ be the lowest value of the temperature during the cycle. Then we have:

$$\sum_i \frac{Q_i(in)}{T_i} \geq \frac{1}{T_{hottest}} \sum_i Q_i(in) \tag{78}$$

or

$$\sum_i \frac{Q_i(in)}{T_i} \geq \frac{Q_{in}}{T_{hottest}} \tag{79}$$

where Q_{in} is the sum of energy entering the gas via heat. Similarly,

$$\sum_i \frac{Q_j(out)}{T_j} \leq \frac{1}{T_{coldest}} \sum_i Q_j(out) \tag{80}$$

or

$$\sum_i \frac{Q_j(out)}{T_j} \leq \frac{Q_{out}}{T_{coldest}} \tag{81}$$

where Q_{out} is the sum of energy leaving the gas via heat. Putting these equations together gives

$$\frac{Q_{in}}{T_{hottest}} \leq \sum \frac{Q_i(in)}{T_i} = \sum \frac{Q_j(out)}{T_j} \leq \frac{Q_{out}}{T_{coldest}} \tag{82}$$

This inequality can be re-written

$$\frac{Q_{out}}{Q_{in}} \geq \frac{T_{coldest}}{T_{hottest}} \tag{83}$$

Since the efficiency $\epsilon = 1 - Q_{out}/Q_{in}$, we have

$$\epsilon \leq 1 - \frac{T_{coldest}}{T_{hottest}} \tag{84}$$

From these inequalities, one can see how to obtain the maximum efficiency. The equal sign will hold if all the energy transfered in (Q_{in}) is done so at the hottest temperature, and all the energy transfered out (Q_{out}) is done at the lowest temperature. The cycle that accomplishes this is a cycle that has two isothermal processes and two adiabatic processes. Such a cycle is called a **Carnot Cycle**. For a Carnot cycle, the efficiency ϵ_{Carnot} is

$$\epsilon_{Carnot} = 1 - \frac{T_{cold}}{T_{hot}} \tag{85}$$

where T_{hot} is the temperature of the hot isothermal and T_{cold} is the temperature of the cold isothermal. $Q = 0$ on the adiabatic legs of the cycle. The Carnot cycle is the most efficient engine operating between the hottest and coldest temperatures.

The meaning of entropy

Previously we derived an expression for the difference in entropy between two states:

$$S(b) - S(a) = \int_a^b \frac{dQ}{T} \tag{86}$$

Note: the integral gives the same value for any path taken from state a to b. Although we derived this for an ideal gas, it holds for any substance. In evaluating the right side, usually T changes as energy is added or subtracted from the system, so one usually needs to integrate. Since ΔQ is related to ΔT via the heat capacity C: $dQ = CdT$, the entropy difference equation can be written as

$$S(b) - S(a) = \int_a^b \frac{C(T)dT}{T} \tag{87}$$

where $C(T)$ is the heat capacity and may depend on the temperature T. If the system changes from $a \to b$ such that C is a constant, then $C(T) = C$ factors out of the integral:

$$S(b) - S(a) = C \int_a^b \frac{dT}{T} = C\ ln(\frac{T_b}{T_a}) \tag{88}$$

For solids and liquids, $C = mc_v$ where c_v is the specific heat capacity. For gases $C = nc_v$ or $C = nc_p$ depending if the process is isometric or isobaric.

Since entropy is heat/temperature, is there a simple connection between the direction of energy flow and entropy change? Yes there is. Consider two systems, one at temperature T_H (hot) and the other at temperature T_C (cold), where $T_H > T_C$. If a small amount of energy ΔQ flows from the hot system to the colder one, the hot system loses entropy equal to $\Delta Q/T_H$. The cold system gains entropy equal to $\Delta Q/T_C$. The net entropy change of the two systems together is

$$\Delta S_{net} = \frac{\Delta Q}{T_C} - \frac{\Delta Q}{T_H} > 0 \tag{89}$$

The sum is greater than zero since $T_C < T_H$. If on the other hand, energy were to flow from the cold system to the hot one, the net entropy change of the two systems together would be

$$\Delta S_{net} = \frac{\Delta Q}{T_H} - \frac{\Delta Q}{T_C} < 0 \tag{90}$$

Thus, it appears that when energy is transfered in the form of heat, the direction of the transfer is such that the net entropy of the two (or more) systems increases. Entropy somehow is related to the direction of energy transfer. The second law of thermodynamics states this more precisely:

Second Law of Thermodynamics: When an isolated system undergoes a change, the entropy of the system can only increase or remain the same.

We know that entropy is a state function and that it is somehow related to the direction of thermodynamic change, but specifically what is it a measure of? Since we have a working model of a monatomic gas, lets determine how the entropy depends on its macroscopic quantities. Suppose we have n moles of a monatomic gas. Let state a have a pressure P_a, a volume V_a, and a temperature $T_a = (P_aV_a)/(nR)$. Let state b have a pressure P_b, a volume V_b, and a temperature $T_b = (P_bV_b)/(nR)$. Let the process from $a \rightarrow b$ be in two parts: an isothermal followed by an isometric. For the isothermal, the temperature is constant at T_a:

$$\Delta S_{isothermal} = \int \frac{dQ}{T} = \frac{Q}{T_a} \tag{91}$$

since T_a factors out of the integral. Q is the net heat, and is equal to the work W done since $\Delta U = 0$ for an isothermal process. So we have

$$\begin{aligned}
\Delta S_{isothermal} &= \frac{W}{T_a} \\
&= \frac{1}{T_a}\int PdV \\
&= \frac{1}{T_a}\int \frac{nRT_a dV}{V} \\
\Delta S_{isothermal} &= nR\, ln\frac{V_b}{V_a}
\end{aligned}$$

For the isometric leg, $\Delta Q = (3/2)nR\Delta T$. The entropy change for this section is

$$\begin{aligned}
\Delta S_{isometric} &= \int \frac{3nR}{2}\frac{dT}{T} \\
&= \frac{3nR}{2} ln\frac{T_b}{T_a}
\end{aligned}$$

Adding the two pieces together, we have for the entropy difference between the states a and b for an ideal monatomic gas:

$$S(b) - S(a) = nR(ln\frac{V_b}{V_a} + \frac{3}{2}ln\frac{T_b}{T_a}) \tag{92}$$

Since the temperature is proportional to the total internal energy U, $(T_b/T_a) = (U_b/U_a)$:

$$S(b) - S(a) = nR(ln\frac{V_b}{V_a} + \frac{3}{2}ln\frac{U_b}{U_a}) \tag{93}$$

in terms of the energy U. We can examine this equation to see what the **entropy** depends on for a **monatomic gas**:

Energy dependence: The entropy is proportional to the log of the energy U of the gas (if n and V are constant). Entropy increases with energy, via the log.

Volume dependence: The entropy is proportional to the log of the volume V of the gas (if n and U are constant).

The energy dependence gives us a relationship between entropy, energy and temperature. If we differentiate S with respect to U,

$$\begin{aligned}\frac{\partial S}{\partial U} &= \frac{3nR}{2U}\\ \frac{\partial S}{\partial U} &= \frac{1}{T}\end{aligned}$$

since $U = (3/2)nRT$ for a monatomic gas. As we mention in the last paragraph (without proof), this relationship can be derived using statistical physics and can be used to define temperature.

The volume dependence is interesting. If the volume of the gas gets larger, with no change in the energy, the entropy increases. Consider a container insulated from the "outside" with two chambers inside. Suppose the gas can travel from one chamber to the other only through a valve. Suppose the gas starts in one chamber with the valve closed, and the other chamber is a vacuum. If the valve is opened, the gas can move to the other chamber and after a while both chambers will be occupied by the gas. The energy of the gas did not change $\Delta U = 0$. The temperature didn't change. However, the entropy increased by an amount $nR\, ln2$.

For a monatomic gas, entropy has something to do with the volume that the gas can move around in. The true meaning of entropy was discovered by Ludwig Boltzmann (1844-1906). He realized that entropy is related to the number of possible configurations of a system. He started a new field of physics called **Statistical Physics**, and revolutionized our treatment of thermodynamics. Statistical physics is a course of its own and usually taught in the senior year (Phy407).

Boltzmann defined a function $\Omega(U)$, which equals the number of different ways that a system can arrange itself with total energy U. Entropy S is related to Ω as

$$S = k\, ln(\Omega) \tag{94}$$

where k is Boltzmann's constant. In statistical mechanics, the temperature of a system is defined by

$$\frac{1}{T} \equiv \frac{\partial S}{\partial U} \tag{95}$$

This definition of temperature is universal. It works for any system. For an ideal gas, this definition for temperature results in temperature being proportional to U. Serendipitously one obtains the same temperature using a constant-volume ideal-gas thermometer, for which temperature was initially defined proportional to pressure and later (using the kinetic theory) found to also be proportional to U.

Summary of Some Processes

The simplist way to find ΔU, Q, W_{by}, and ΔS for a reversible process is to do the following. *First* determine ΔU, which equals $\Delta U = (3/2)nR\Delta T$ or $\Delta U = (3/2)\Delta(PV)$ for a monatomic gas. For a diatomic gas at room temperature just replace the (3/2) with (5/2). *Second* determine W_{by} by finding the **area under the curve in the P-V plane**. W_{by} is the same for any type of gas. *Third* find Q, which is just $Q = \Delta U + W_{by}$. This is true for any type of gas. *Finally* determine ΔS by carrying out the integral $\Delta S = \int (dQ)/T$, where T is the temperature (in Kelvin) at which the incremental heat energy dQ is transfered.

Isothermal Process

For an isothermal process, $\Delta T = 0$ and hence $\Delta U = 0$. This is true for both a monatomic and diatomic gas. If the process is reversible, then $PV = nRT_0$ during the process, where T_0 is the constant temperature. The work done by the gas is then $W_{by} = \int PdV = nRT_0 \int (dV)/V$. The integral of $\int dV/V = ln(V)$, and taking the limits from the initial volume V_i to the final volume V_f gives $W_{by} = nRT_0 ln(V_f/V_i)$. This is the work for both a monatomic and a diatomic gas. Since $\Delta U = Q - W_{by}$, we have $Q = W_{by} = nRT_0 ln(V_f/V_i)$. To find the change in entropy for an isothermal process, we need to do the integral $\Delta S = \int (dQ)/T = (1/T_0) \int dQ = Q/T_0$, since the temperature is constant. Using the expression for Q, we have $\Delta S = nRln(V_f/V_i)$. We can summarize our results in the following chart:

Process	W_{by}	Q	ΔU	ΔS
Isothermal	$nRT_0\ ln(V_f/V_i)$	$nRT_0\ ln(V_f/V_i)$	0	$nR\ ln(V_f/V_i)$

for both monatomic and diatomic gases.

Isometric Process

For an isometric process, $\Delta V = 0$, and hence $W_{by} = 0$. Since $W_{by} = 0$, $\Delta U = Q$. The change in internal energy ΔU will depend on ΔT. For a monatomic gas, $\Delta U = (3/2)nR\Delta T$ and for a diatomic gas (at room temperature) $\Delta U = (5/2)nR\Delta T$. We can also express ΔU in terms of the change in the product of PV, since $nRT = PV$.

In terms of PV, we have $\Delta U = (3/2)\Delta(PV)$ for a monatomic gas, and $\Delta U = (5/2)\Delta(PV)$ for a diatomic gas at room temperature.

To find the change in entropy for an isometric process, we need to carry out the integral $\Delta S = \int(dQ)/T$. For a monatomic gas, $\Delta Q = (3/2)nR\Delta T$. Thus, $\Delta S = (3/2)nR\int(dT)/T = (3/2)nR\ ln(T_f/T_i)$. For a diatomic gas, $\Delta Q = (5/2)nR\Delta T$. In this case, the change in entropy is $\Delta S = (5/2)nR\ ln(T_f/T_i)$. We can summarize these results in the following charts:

Process	W_{by}	Q	ΔU	ΔS
Isometric	0	$(3/2)\Delta(PV)$	$(3/2)\Delta(PV)$	$(3/2)nR\ ln(T_f/T_i)$

for a monatomic gas. For a diatomic gas, the results are

Process	W_{by}	Q	ΔU	ΔS
Isometric	0	$(5/2)\Delta(PV)$	$(5/2)\Delta(PV)$	$(5/2)nR\ ln(T_f/T_i)$

Adiabatic Processes

For an adiabatic process there is no "heat" exchange, $Q = 0$. Thus, $\Delta S = 0$, and $W_{by} = -\Delta U$. For a monatomic gas, $\Delta U = (3/2)nR\Delta T = (3/2)\Delta(PV)$ For a diatomic gas, $\Delta U = (5/2)nR\Delta T = (5/2)\Delta(PV)$. These results can be summarized in following charts:

Process	W_{by}	Q	ΔU	ΔS
Adiabatic	$-(3/2)\Delta(PV)$	0	$(3/2)\Delta(PV)$	0

for a monatomic gas. For a diatomic gas, the results are

Process	W_{by}	Q	ΔU	ΔS
Adiabatic	$-(5/2)\Delta(PV)$	0	$(5/2)\Delta(PV)$	0

Isobaric Processes

For an isobaric process, all the quantities ΔU, Q, W_{by}, and ΔS are non-zero. Let the pressure be P_0, and the initial and final volumes be V_i and V_f. Then $\Delta U = (3/2)nR\Delta T = (3/2)\Delta(PV) = (3/2)P_0(V_f - V_i)$. $W_{by} = P_0(V_f - V_i)$. The "heat" energy transfer is $Q = \Delta U + W_{by} = (5/2)P_0(V_f - V_i)$, since $(3/2) + 1 = (5/2)$. The change in entropy is $\Delta S = \int(dQ)/T = \int(5/2)nR(dT)/T$. Evaluating the integral gives $\Delta S = (5/2)nR\ ln(T_f/T_i)$, which equals $\Delta S = (5/2)nR\ ln(V_f/V_i)$, since $(T_f/T_i) = (V_f/V_i)$ for an isobaric process. These results can be summarized in the following charts:

Process	W_{by}	Q	ΔU	ΔS
Isobaric	$P_0(V_f - V_i)$	$(5/2)P_0(V_f - V_i)$	$(3/2)P_0(V_f - V_i)$	$(5/2)nR\, ln(V_f/V_i)$

for a monatomic gas. For a diatomic gas, the results are

Process	W_{by}	Q	ΔU	ΔS
Isobaric	$P_0(V_f - V_i)$	$(7/2)P_0(V_f - V_i)$	$(5/2)P_0(V_f - V_i)$	$(7/2)nR\, ln(V_f/V_i)$