CHAPTER ONE

Thermodynamics

Introduction

Thermodynamics

is a science of the relationship between **heat, work, temperature,** and **energy**. In broad terms, thermodynamics deals with the transfer of energy from one place to another and from one form to another. The key concept is that heat is a form of energy corresponding to a definite amount of mechanical work.

1.1 Thermal equilibrium and definition of temperature

Atoms and Moles

The term mole is used to represent large number of atoms or molecules just the way a dozen is used to represent 12 things. A dozen eggs means 12 eggs.

Moles of particles work similarly. One mole of Helium gas means 6.02×10^{23} particles of Helium gas. Or one mole of eggs would mean 6.02×10^{23} eggs. The number 6.02×10^{23} is called Avogadro's number (N_A). From the dozen analogy if there are 'n' moles of particles to know the total number of particles all we have to do is:

$$N = nN_A \quad \text{where} \quad \text{N- no. of particles}$$

$$\text{n- no. of moles}$$

$$\text{NA- Avogadro's no.}$$

One mole of water contains 6.02×10^{23} molecules of water. This means there are 6.02×10^{23} Oxygen atoms and 1.20×10^{24} Hydrogen atoms (2 Hydrogen atoms in each water molecule).

The dozen analogy works once more for the concept of molar mass. Three dozen eggs means 36(3×12). If the price of a dozen egg is 60 birr, the price of a single egg 5 birr (60/12).

Molar mass of a substance is the mass of one mole of that substance. To find the mass of each particle, all we have to do is to divide the molar mass by Avogadro's no. i.e. ,

$$m_P = M/N_A \quad \text{where } m_p\text{-mass of one particle of a substance}$$

$$M\text{- molar mass of the substance}$$

The mass of n moles of a substance is:

$$m = nM \qquad \text{(like the price of 3 dozen eggs is 3*60=180 birr)}$$

Temperature

We often associate the concept of temperature with how hot or cold an object feels. Our senses are, however, unreliable. Let say we have three bottles filled with water. A is ice, B is lukewarm and C is boiling. Relative to C, B is cold but relative to A, B is hot. Is B hot or cold?

So, we need a reliable measure of hotness and coldness hence Temperature.

An important way to define temperature is using the particle model of matter. The particle model of matter is a way of visualizing what individual particles are doing inside a substance.

Particles of matter are always in random motion. In solids, they are vibrating. In liquids and gases, they are moving more freely. Consequently, particles collide with their neighbors. Because of this collision, energy is distributed throughout the substance.

Temperature is the measure of how fast, on average, the particles of that substance are moving. The faster the particles are vibrating, the higher the temperature of the substance is.

Thus, temperature can be defined as the measure of the average random kinetic energy of particles in a body.

Suppose two objects, one hot and one cold, are in thermal contact. Energy is transferred from the hotter object to the colder object. For example, when hot water and cold water are mixed in a bath tub, energy is transferred form the hot water to the cold water. Eventually, they reach to some intermediate temperature.

We know from the particle model of matter, this is the case because the particles in the hotter body are moving faster than that of the colder body. First, the particles at the boundary collide and then through many collisions the energy is distributed throughout the bodies until then reach a point where there will not be any energy transfer between the two bodies. This situation is called **thermal equilibrium**. The net transfer of thermal energy from the hotter body to the colder body is called **heating**.

This is the only way that the word heat can be used. A body does not **contain** or **possess** heat.

The zeroth law of thermodynamics (the law of equilibrium)

It can be stated as:

If objects A and B are separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.

This is the way thermometers work and this law also gives us a way to define temperature as a property that determines whether an object is in thermal equilibrium with other objects. Two bodies that are in thermal equilibrium with each other are at the same temperature. Temperature thus dictates the direction of heat transfer. Heat flows from a body with a higher temperature to a body with a lower temperature.

Temperature scales

Fahrenheit scale:

This is a common temperature scale in everyday use in the United States. This scale sets the temperature of the ice point of water 32 F and the temperature of steam point at 212 F.

Celsius scale:

Defines the ice point of water (at atmospheric pressure) to be 0 ºC and the steam point of water to be 100 ºC.

Both of the above scales are based on assigning random melting and boiling points associated with one particular substance, water, on one particular planet, Earth.

Kelvin scale:

This is a scale based on a **true zero** value of temperature. It sets -273.15 °C, the temperature at which all the random motion of particles in a substance cease, as its zero point, 0 K. The second reference temperature for this scale was chosen as the triple point of water. This is a single combination of temperature and pressure at which all the three states of water coexist in equilibrium. This point was defined to be 273.16 K.

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The relationship between the kelvin and Celsius scale is given by:

$T_K = T_C + 273.15$

The Kelvin scale is also referred to as the **absolute thermodynamic scale**.

Caution:

If you encounter an equation that calls for a temperature T or that involves a ratio of temperatures, you MUST convert all temperatures to Kelvin. If an equation contains a change in temperature, using Celsius temperature will also work, but it is always safe to convert temperatures to the Kelvin scale.

Phase of matter

A phase of matter is when all the physical properties within a material are **uniform**.

State and phase of matter are closely related concepts. States of matter are based on some large scale properties of phases of matter. Look at the figure below

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Changing the pressure or temperature of a substance will affect its phase. This can be seen from a temperature vs pressure graph known as phase diagram.

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There is an important difference between the phase diagram of many substances and phase diagram of water. In water's diagram, the slope of the line between the solid and liquid states is negative while it is positive for many substances. The

reason is that water is an unusual substance in that its solid state (ice) is **less dense** than its liquid state.

As can be seen from the diagram, all substances have multiple boiling and melting points based on the surrounding pressure. For example, when we say the melting point of water is 0 C what we mean is the melting point of water at standard atmospheric pressure is 0C. Water melts at different temperatures based on the surrounding pressure.

Two points are to be noted from the phase diagram.

Triple point:

It is a point with single temperature and pressure for each substance where all the three states of matter coexist in thermal equilibrium. For water, this point is at 611.2 Pa and 0.01 °C.

Critical point:

It is a point above which the gas and liquid phases merge and clear phase boundaries cease to exist. The substance forms supercritical fluid. For water this point occurs at around 647 K & 22MPa. Above the critical temperature it is not possible to form a liquid regardless of any increase in pressure.

1.2 Work, heat and the first law of thermodynamics

Historical notes

Suppose a gas in a cylinder with a movable piston is given to you. And you were told to increase the temperature of the gas. What would you do?

You can do two things to achieve the increase in temperature.

The first one is pretty obvious. Fix the piston at the position where it was given to you and heat the cylinder using a candle. The number of collisions between particles increase, the particles of the gas start to move faster.

The second way is to compress the gas by pushing the piston. The volume of the gas decreases; collisions become more frequent; the speeds of the gas particles increase; the temperature of the gas increases.

The first law of thermodynamics, which is a special case of the law of conservation of energy, deals with these types of energy dynamics. But, before stating the law, an important term needs to be clearly defined.

What exactly is internal energy?

In the above example, the temperature of the gas is closely related to its internal energy. The temperature of the gas is increased means the gas now has higher internal energy.

Internal energy is all the energy of a system that is associated with its microscopic components -atoms and molecules. Thus, if the particles of a system has higher temperature, the system is said to possess higher internal energy.

But kinetic energy is not all the energy associated with particles in a system. There is also potential energy. This is the energy due to the interaction between particles in a system. Phase change is good example. When there is a phase change, for example, when you heat liquid water at 100 C to boil it, this phase change occurs at constant temperature, i.e., liquid water at 100 C changes to steam at 100 C (Note that addition of heat does not always guarantee increase in temperature, phase change is a good example.) Since there is no change in the temperature of water, does this mean its internal energy is also constant? No! The internal energy increases not because the temperature increases, but because work was done on individual molecules to move them apart against their intermolecular attraction.

Two final notes are important

1. It is usually, but not always, important to associate the internal energy of a system with its temperature.
2. Internal energy is concerned with energy 'internal' to the system. For example, if the system, as a whole is moving with a speed v, the energy due to this motion is not included in the system's internal energy.

First law of thermodynamics

It states that

"The increase in internal energy of a system is equal to the sum of the energy entering the system through heating and the work done on the system" Or mathematically

$\Delta U = \Delta Q + \Delta W$ 　　　　　　where ΔU is increase in internal energy

ΔQ is energy entering the system due to heating

ΔW is work done on the system

Some important points to be noted arise from the above formula

1. If you want to increase the internal energy of a system, you can heat the system or do work on the system or both.
2. Energy can enter the system through heating(in this case, ΔQ is positive) or energy can leave the system through heating if the system is hotter than its surroundings (in this case, ΔQ is negative)
3. Work can be done on the system externally (in this case, ΔW is positive) or work can be done by the system (on its surroundings: in which case ΔW becomes negative.) For the example at the beginning of this section, to compress the gas means to do work on the system, which tries to increase the internal energy of the gas. If the gas were allowed to expand, it would lift the piston, work is said to be done by the gas which in effect tries to decrease the internal energy of the gas.
4. The sign convention must be used consistently.

The first law for different thermodynamic processes
Here we use ideal gas in a cylinder to describe the equation of first law of thermodynamics for different processes. We also draw the pressure vs. volume diagram (PV diagram) for each process. It is a very important diagram which helps to find the work done on or by a system. The total work done is the area under p-v diagram.

A. Isochoric
is a process for which the volume of a system remains constant. It is also called an isovolumetric process.
The work done (area under p-v graph) of this process is zero since the gas is neither compressed (work done on the system) nor does it expands (work done by the system)
Thus the first laws equation becomes: $\Delta U = \Delta Q$
Quick quiz: for which of the two figures above is ΔQ positive?
B. Isobaric

is a process for which the pressure of a system remains constant. The p-v diagram for this process is:

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The area under this graph is simply: $\Delta W = p\Delta V$ (area of rectangle)

If the volume of the gas increases, work is done by the system, and ΔW is negative. If the volume of the gas decreases, work is done on the system, and ΔW is positive.

Thus, the first law equation becomes: $\Delta U = \Delta Q - p\Delta V$

Quick quiz: show that the expression $p\Delta V$ is equivalent to the mechanical work done $W = F\Delta x$.

C. Adiabatic

Is a process for which there is no heat transfer into or out of the system. Thus $\Delta Q = 0$. The p-v diagram for adiabatic process is

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Quick quiz: for which of the two figures above is the temperature of the gas increasing? A. for a B. for b C. cannot be known

But how can we achieve adiabatic process in reality?

*As discussed earlier, heat is transferred between two bodies due to temperature difference. If a gas is compressed rapidly, there is negligible time in which energy transfer to the surroundings by heating can occur, and the process is nearly adiabatic. Of course after the compression is complete, the temperature gradient between the system and its surroundings will result in energy transfer from the system, resulting in a decrease in internal energy of the gas. In general, rapid expansion and rapid compression are considered as nearly adiabatic.

Insulating a system is another way we can achieve an adiabatic process.

D. Isothermal

Is a process for which the temperature of the system remains constant.

The p-v diagram for this process is

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For an ideal gas the internal energy depends only on temperature since there are no intermolecular forces except during collisions.

Thus, $\Delta U = 0$ for an isothermal for an isothermal thermal process. The first law equation becomes: $0 = \Delta Q + \Delta W$

$$\Delta Q = -\Delta W$$

Quick quiz: for which of the two figures above does energy leave the system through heating? A. for a B. for b C. cannot be known

How can we achieve an isothermal process practically?

If a process occurs extremely slowly (also called quasistatically), there will be heat flow into or out of the system at each point so that the system maintains its temperature. Thus, very slow processes are considered to be nearly isothermal.

For a cyclic process (a process for which the system returns to its initial state) $\Delta U=0$. $U_{AB}+U_{BA}=0$

Molar heat capacity and Mayer's equation

Molar heat capacity of a substance is the amount of energy that must be added in the form of heat to one mole of the substance in order to cause an increase of one unit in its temperature. It has units of J/molK.

For example, if the molar heat capacity of nitrogen is said to be 20.7 J/molK, this means we need to add 20.7 J of energy to 1 mol of Nitrogen to increase its temperature by 1 K. But the amount of energy required is different depending on the conditions under which the heating occurs. For example, in Nitrogen's case 20.7 J of energy is required if we are about to heat Nitrogen at constant volume. Thus we need to define two quantities: molar heat capacity at constant volume (C_v) and molar heat capacity at constant pressure (C_p).

When n moles of a gas are heated resulting a temperature rise of T, we can write:

$C_p=\Delta Q_p/n\Delta T$ and $C_v=\Delta Q_v/n\Delta T$

ΔQ_p- energy transferred to the gas at constant pressure

ΔQ_v- energy transferred to the gas at constant volume

From the first law of thermodynamics for isobaric process we know that:

$\Delta U=\Delta Q_p-p\Delta v \Longrightarrow \Delta Q_p=\Delta U+p\Delta v$………..(1)

From the first law of thermodynamics isochoric process we know that:

$\Delta U=\Delta Q_v \Longrightarrow \Delta Q_v=\Delta U$……..(2)

From the above equations we can see that to bring about the same change in internal energy (the same change in temperature) we need more energy to add at constant pressure than at constant volume. This is because in the constant volume process the heat we added is only used to increase the internal energy, but in the constant pressure process the heat we added is used to increase the internal energy and do work on the surroundings(the gas expands). Therefore it is always true that

$C_p > C_v$

From 1 and 2:

$\Delta Q_p = Q_v + p\Delta v \Rightarrow C_p n\Delta T = C_v n\Delta T + p\Delta v$

From the ideal gas equation (to be derived in the next section), $pv=nRT$ where $R=8.3$ J/molK, the molar gas constant

$C_p n\Delta T = C_v n\Delta T + nR\Delta T$

$C_p = C_v + R$

$C_p - C_v = R$…..Mayer's Equation

The above expression is true for ideal gases.

The change in internal energy of an ideal gas when heated at constant volume is given by:

$\Delta U = 3/2 nR\Delta T$………This will be shown in the next section

From $\Delta Q_v = \Delta U$

$nC_v\Delta T = 3/2 nR\Delta T$

$C_v = 3/2 R$

Substituting in $C_p = C_v + R$

$C_p = 5/2 R$

Then

$C_p/C_v = 5/3 = d$, the ratio is given the symbol d

For diatomic gases like oxygen and nitrogen $d = 7/5$

- The quantity d is important to relate the state variables p,v&t for reversible adiabatic process.

For a reversible adiabatic process, it is true that:

TV^{d-1}=constant & PV^d=constant

For a reversible adiabatic process that goes from 1 to 2

$T_1V_1^{d-1}=T_2V_2^{d-1}$ & $P_1V_1^d=P_2V_2^d$

A sample of an ideal gas goes through the process shown in the figure below. Form A to B the process is adiabatic, from B to C isobaric with 100kJ of energy entering the system by heat. From C to D, the process is isothermal; from D to A it is isobaric with 150 kJ of energy leaving the system by heat. Determine the difference in internal energy, U_B-U_A

- Different ways to do work on a system. Electrical …..
- $Q=mc\Delta T$
- Addition of heat doesn't always guarantee an increase in tempreture . eg. Phase change (latent heat)

1.3   Kinetic theory of gases

Why so much focus on gases?

In this chapter we focused on gases to keep the mathematics relatively simple since in gases the interactions between molecules are much weaker than they are in liquids and solids. A gas consists of atoms that fill their container's volume and exert pressure on the container's walls. We can usually assign a temperature to such a contained gas. These three variables associated with a gas- volume, pressure and temperature- are all a consequence of the motion of the atoms.

Volume – is a result of the freedom the atoms have to spread throughout the container.

Pressure – is a result of the collisions of the atoms with the container's walls

Temperature – average kinetic energy of the atoms.

The kinetic theory of gases relates the motions of the atoms (a microscopic quantity) to the volume, pressure and temperature of the gases (macroscopic quantities). For example, it makes us able to answer questions like how fast the molecules in the air are are moving right now by only having the knowledge of macroscopic quantities like the surrounding temperature and pressure.

What are the gas laws and the ideal gas equation?

Our goal in this section is to explain the macroscopic properties of a gas- such as its pressure and temperature- in terms of the behavior of the molecules that make it up. However, there is an immediate problem: which gas? Should it be hydrogen, oxygen, or methane or perhaps uranium hexafluoride?

 Experiments have found that if we confine 1 mol sample of various gases in boxes of identical volume and hold the gases at the same temperature, then their measured pressure are almost the same! What is more? At lower densities the differences tend to disappear! Such a low-density gas is commonly referred as an ideal gas.

An ideal gas is not a real gas, but it is a good approximation for all real gases unless the pressure is not too high or the temperature is not too low, the conditions under which the gas liquefies.

The relationship between the pressure, volume and temperature of an ideal gas is given by the ideal gas equation. It is derived from the empirical (experimental) gas laws.

> Note: Low density implies molecules are fast enough apart that they do not interact with one another.

Suppose an ideal gas is confined to a cylindrical container whose volume can be varied by means of a movable piston as shown in the **figure**. If we assume the cylinder does not leak, the mass (or the no. of moles) of the gas remains constant. For such a system, experiments provide the following information.

- When a gas is kept at a constant temperature, its pressure is inversely proportional to the volume.
  PV=constant (if T is constant) ---- **Boyle's law**
- When pressure of the gas is kept constant, the volume is directly proportional to the temperature.

V/T=constant (if P is constant) --- **Charles' law**

- When the volume of the gas is kept constant, the pressure is directly proportional to the temperature.
  P/T=constant (if V is constant) --- **Gay-Lussac's law** or **Pressure law**

These observations are summarized by the equation of state for an ideal gas:

PV=nRT , the ideal gas equation
Where n- no. of moles of the gas
R- 8.3 J/mol.K, the universal gas constant

Dalton's law of partial pressures

Avogadro's law states that "equal volumes of all gases at the same temperature and pressure contain the same number of molecules." This can be explained from the ideal gas equation. Rearranging the equation gives n=PV/RT. So if P,V,& T are equal for two gases, then the no. of moles of the two gases is also equal.

Suppose a mixture of Hydrogen and Oxygen gases is

Dalton's law of partial pressure explains how a mixture of gases behaves in terms of the pressure it exerts. The law states that "the total pressure of a mixture of gases, which do not react chemically, is equal to the sum of the partial pressures, i.e., to the sum of the pressure that each gas would exert if it alone occupied the volume contacting the mixture."

Suppose a mixture of two gases are contained in a container of volume V. Let the no. of moles of the first gas be n_1 and the pressure it would exert if it were alone in the container (without gas 2) be p_1. Then define n_2 and p_2 similarly for gas 2. If the mixture is in thermal equilibrium at temperature T, then:

$P_1V=n_1RT$ …..(1)

$P_2V=n_2RT$ …(2)

Dividing (1) by (2)

$P_1V/ P_2V =n_1RT/ n_2RT$

$P_1/P_2=n_1/n_2$

$P_1=n_1/n_2\ P_2$

From Dalton's law

$P = P_1 + P_2$

$P = n_1/n_2\, P_2 + P_2 \implies P_2 = (n_2/n_1 + n_2)\, P$

The kinetic theory of gases

Here is our first kinetic theory problem. Let n moles of an ideal gas be confined in a rectangular box of volume. the walls of the box are held at temperature T. what is the connection between the pressure P exerts by the gas on the walls and the speed of the molecules?

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Lets ignore collisions of molecules with one another and consider only elastic collisions with the walls.

Step 1:

To start with, consider a single particle, of mass m and velocity c, that is about to collide with the shaded wall.

GIF

The particle collides elastically with the shaded wall and rebounds with a velocity –c. the wall will cause a change in the particles momentum of 2mc.(momentum =mv)

Step 2:

The particle will hit the shaded wall repeatedly, exerting a force on the shaded wall many times but only for a short duration each time.

How long is the time between two successive collisions? Once the particle hits the shaded wall it needs to travel a length l to hit the opposite side and then a length l to hit the shaded wall gain, a total of 2l. Since the speed of the particle is c, the time between two successive collisions is: t=2l/c

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Step 3:

From Newton's second law, force is equal to the change in momentum divided by the time taken. Therefore, the average force the wall exerts on the particle becomes

2mc//2l/c=mc2/l

Step 4:

From Newton's third law, the force the particle exerts on the wall is equal in magnitude but opposite in direction to the force the wall exerts on the particle. The average force exerted on the wall over a series of impacts therefore equals mc2/l(equal in magnitude with step 3)

Step 5: what pressure does the particle exerts on the shaded wall on average?

Pressure is equal to force divided by area and the area of the shaded wall is wh. The average pressure exerted by the particle on the wall therefore becomes:

mc2/l//wh=mc2/lwh, but lwh=V, where V is the volume of the box

So the average pressure can be written as **mc2/V**

Step 6:

In reality, there will be N particles in the box moving in random directions. On average, one-third of the particles collide with the shaded wall the opposite wall: one-third of the particles collide with the top and the bottom walls and one-third of the particles will collide with the front and the back walls. If one particles exerts an average pressure of mc2/V, the total average pressure on the shaded wall becomes:

N/3*mc2/V=Nmc2/3V

The above formula is independent of the direction of the particles motion. Thus, first we can say it represents the total average pressure on any of the walls. Second, we can talk about the particles' speed instead of its velocity.

Step 7:

If one particle has a mass m, then N particles have a total mass of Nm. Since density is mass divided by volume, the density of the gas becomes:

p..=Nm/V the total average pressure then becomes: p..c2/3

Step 8:

We need one friend, important alteration. There are many particles in the gas and all of them don't have equal speeds, c. So to get the mean pressure what we have to use is what is called the **mean squared speed**, $\langle c^2 \rangle$.

$P = 1/3 p .. \langle c^2 \rangle$

Mean squared speed: if there are N particle and if particle 1 has a speed c1, particle 2 has a speed c2,…, particle N has a speed cn, then:

$\langle c^2 \rangle = c1^2 + c2^2 + c3^2 + \dots + cN^2 // N$

We don't usually use this formula in our calculations but it gives us a sense of what is meant by mean squared speed.

The square root of mean squared speed is called the rms speed. i.e.
$Crms = r \langle c^2 \rangle$
Here we have related the pressure of the ideal gas , a macroscopic quality, to the mean square speed of all the particles in the gas, microscopic quantity.

Summary of the assumptions make in the kinetic theory of gases

1. There is no interaction between particles and between particles and the wall except during collision. The internal energy is make up of random kinetic energy of particles only; no potential energy element.
2. All collisions are perfectly elastic (no loss of kinetic energy in collision)
3. The volume occupied by the particle is negligible compared to the volumeof the gas as a whole.
4. The distribution of velocities of particles is random.
5. Newton's laws can be applied to all collisions.

After the $p = 1/3 p .. \langle c^2 \rangle$ formula,

$Crms = r3p/p.. = r3VP/Nm$ ……..from $PV = nRT$

$Crms = r3nRT/Nm = r3RT/M$

Brownian motion and diffusion

The Scottish botanist Robert Brown observed that pollen grains suspended in water would 'jiggle' around when seen under a microscope. This random movement of particles is called Brownian motion.

GIF

The cause for this motion is that the particle in the fluid being constantly bombarded from all sides by molecules of the fluid. One useful parameter to describe this random motions is the mean free path d of the particle, d. Mean free path is the average distance covered by a molecule between collisions. If the temperature of a gas is high or the pressure of a gas is high, then particles are moving faster and collisions are frequesnt. Therefore=, the mean free pathe becomes shorter. i.e. after the particle covers a short distance it collides with another particle.

It was Einstein who first come up with an acceptable mathematical model that these movements can be predicted directly from the kinetic model of thermal equilibrium. He has also provided a mathematical explanation for the process of diffusion, the process by which particles in a fluid spread from a region of high concentration to a lower one.

Quick quizzes

1. How fast are molecules in the air moving right now? Take density of air at approximately 25 c as 1.18 Kg/m3 and atmospheric pressure at sea level as 101 KPa.
2. If molecules move so fast, why does it take as long as a minute or so before you can smell perfume when someone opens a bottle a room.

Graham's law of diffusion

The rms speed of molecules has an effect on how fast they diffuse through a medium. Higher rms speed of molecules means higher rate of diffusion. Graham's law states that "the rate of diffusion of a gas is inversely proportional to the square root of its density".

Suppose two gases are given at the same temperature and pressure with equal volume. From Avogadro's law the two gases contain the same no. of molecules.

Density is mass divided by volume:

d..1=m1/V, d..2=m2/V since V is the same m1/d..1=m2/d..2

We know that the kinetic energy of particles depend only on the temperature since both gases are at the same average temperature, they have equal average KE.

$.5m_1<C_1>=.5m_2<C_2>$

$<C_1^2>/<C_2^2>=m_2/m_1=d_{..1}/d_{..2}$ then $C_{1rms}/C_{2rms}=rd_{..2}/d_{..1}$

The rate of diffusion in a gas, which depends on rms speed of molecules is inversely proportional to the square root of the density of the gas.

Kinetic energy and Internal energy

How can we relate the average kinetic energy of a particle to the macroscopic quantities?

We know that $P=1/3d_{..}<C^2>=1/3Nm<c^2>/V$ then $PV=1/3Nm<c^2>$

From the ideal gas equation: $PV=nRT$

$nRT=1/3Nm<c^2>$

The average KE $<E_k>$ is given by: $<E_k>=1/2m<C^2>$

$3nRT/N=m<C^2>$ then $1/2m<c^2>=3/2nRT/N=3/2N/N_aRT/N=3/2RT/N_A$

$R/N_a=K$……Boltzmann constant, $k=1.3*10^{-23}J/K$

….

This relationship only holds for an ideal gas. The average random kinetic energy of an ideal gas depends only on the Kelvin temperature.

For an ideal gas the internal energy is the sum of all random kinetic energies of its particles. Therefore if there are N particles, then the internal energy is:

….. this is the formula we use in the previous section

For one mole of gas, the internal energy becomes

…..

1.4 Second law of thermodynamics, efficiency and entropy

If you were to wrap your hands around a cup of hot coffee, you would be astonished if your hands got cooler and the cup got warmer. But why is that? What is the problem if the same amount of energy that is lost from your hands is added

to the coffee? Obviously, in the process, the energy of the closed system is conserved(the first law of thermodynamics is obliged). But we know that things do not happen this way in reality. A tennis ball on the ground never gathers internal energy from the ground and begins boucing on its own. Such processes are irreversible; that is, they are processes that occur naturally in one direction only.

The second law of thermodynamics offers an answer to such questions. We will state the second law of thermodynamics in different forms in the coming two sections. But in all its forms, the second law states impossibility; which processes are not possible or in which direction processes must proceed. You might think understanding why time has direction and why one-way processes are irreversible has nothing to do with practical issues of everyday life. It is in fact at the heart of any engine, such as a car engine, because it determines how well an engine can run.

The key to understanding why one-way processes cannot be reversed involves a quantity known as entropy.

Entropy and the second law of thermodynamics

Changes in energy within a closed system donot set the direction of irreversible processes. This is because, as we have dicussed above, things that would have obeyed the first law of thermodynamics had they happended do not happen in reality. Rather, the direction is set by another property, the change in entropy of the system.

Entropy is a measure of the amount of disorder in a system. It is related to the no. of ways that the system may be arranged. If there are more no. of ways a system ca be arranged. Then we say the entropy of the system is higher. To explain this idea, consider five molecules in a container which are confined to the left hand side of the container by a cover slide as shown in the figure below.

Now imagine the cover slide is removed and the molecules are allowed to diffuse. What would you expect? We would normally expect the molecules to be evenly distributed among the left and right hand side of the container. There are actually 32 ways (2^5) the molecules can be distributed (can you do the math?). One is, all the five molecules to be on the left hand side; the other is all the five molecules to be on the right hand side; then one molecule on the left hand side on the RHS (There are five different ways this can happen depending on which of the five

molecules is on the LHS). Two molecules on the LHS and three on the RHS; so on.

Now the important question is, which of the two systems does have a higher entropy? Is it the system with the molecules confined to the left hand side by the cover slide, or is it the system with the cover slide removed? From the definition of entropy, it is the system with the cover slide removed that has a higher entropy. This is because there is only one way the molecules can be arranged with the cover slide (namely, all molecules are on the left side), but there are 32 ways the molecules can be arranged when it is removed.

The second law of thermodynamics states that:

"No process is possible in which there is an overall decrease in the entropy of the universe." (Entropy statement of the second law of thermodynamics).

If it were 1 mol of a gas that was confined in the left side by the coverside, which is a more realistic situation, then there would be unimaginable high no. of possible arrangements (namely, $2^{6.02*10^{23}}$) after the cover slide is removed. Thus the increase in entropy is very high when the cover slide is removed. What is the probability that we find all the molecules on the left side? It is 1 in $2^{6.02*10^{23}}$ which is extremely improbable.

But what if we place all molecules to the left side(either by compressing the gas or by picking each individual molecule) and seal it? Does not that account for a decrease in entropy, and hence, an example for where the second law fails? No! it is true that the entropy of the gas decreases because there are less number of ways the system can arrange itself. But the gas alone is not a close system now. The person (agent) doing the mechanical work is involved too. By doing work on the gas, an increase in entropy (larger than the decrease in entropy of the gas) is caused elsewhere. Thus, in effect, the entropy of the universe has increased, and hence, the second law is obeyed.

How is entropy related to energy and heat?

In the early 20th century it was found that atoms can only increase or decrease their energy in set amounts, called quanta. (You might have heard the concept of energy quantized before. It was the German physicist Max Plank who first postulated this ideal to explain black body radiation, and later, Albert Einstein used it to explain a phenomenon called the photoelectric effect). Remember this from grade 11 chemistry?

It is the behavior of quanta, tiny packets of energy, that is similar to the behavior of particles in a gas. It might be helpful to think of the quanta as candies. If the quanta were held by small no. of atoms, then the no. of possible arrangements is small. But nature tends to distribute the candies. Although the total energy (the total number of candies) remain the same, the number of possible arrangements (and therefore entropy) increase when the same nol of quanta are distributed among large no. of atoms. This is why energy in an isolated system tends to spread out over time: the entropy of the system must not decrease.

Why can we not build a power station that is perfectly efficient?

A heat engine, or more simply, an engine, is a device that extracts energy from its environment in the form of heat and does useful work. At the heat of every engine is a working substance. The working substance of a steam engine is, for example, water. And that working substance operates in a cycle. (More on the working principle of engines will come in the next section).

The aim of a heat engine is to take energy in the form of heat from a heat source and convert it to mechanical work. But the second law of thermodynamics puts a limitation to that. It can be stated as

The kelvin-plank statement of the second law of thermodynamics:

> " the complete conversion of energy form a heat source into work is not possible"

> OR alternatively,

> " it is impossible to construct a heat engine, operating in a cycle, that produces more effect other than the input of energy by heat from a reservoir and the performance of an equal amount of work."

Let Q_h be the energy the heat engine absorbs from the heat source and W be output work of the engine. The second law states that W can not be equal to Q_h. Hence heat is extracted from the heat source, its entropy decreases. If that heat is compeletly converted to work, then the overall entropy of the system decreases, which violates the second law. Thus, to offset this decrease, some energy Q_c must be rejected to the environment (to the heat sink).

What process can we reverse and why is this important?

A reversible process is one that can be reversed by means of an infinitesimally small change in a property of the system without a transfer of enery. In a reversible process, a system undergoing the process can be returned to its initial conditions along the same path on a PV diagram, and every point along this path is an equilibrium state. All real processes are irreversible: a reversible process is an idealization. To understand the concept more , let's see two examples, one irreversitble process and one nearly reversible process.

Consider a gas in a thermally insulated container as shown in the figure-----serway.

Membrane separates the gas from a vacuum. When the membrane is punctured, the gas expands freely into the vacuum. This is an adiabatic process since the system is insulated and no work is done by the gas since it's expanding freely ot fill the container. The system has changed because it occupies a greater volume now, but the surroundings have not since there is no heat exchange or work.

For this process to be reversible, we must return the gas to its original volume and temperature without changing the surroundings. If we compress the gas(ourselves or using an engine) the surroundings change because work is being done by an outside agent on the system. In addition, the system changes because the compression increases the temperature of the gas. We can lower the temperature by allowing it to come into contact with an external reservoir. This returns the gas to its original conditions but affects environment again.

Think about this:

> What if we used the energy coming out of the gas to the external reservoir to drive the engine that is used to compress it? Wouldn't the net energy change be zero and the process be considered as reversible?

> (Hint: think of the Kelvin-Plank statement of the second law)

Now consider a gas that is compressed exothermically in a piston-cylinder arrangement in which the gas is in thermal contact with an energy reservoir and we continuously transfer just enough from the gas to the reservoir to keep the temperature constant. Imagine that the gas is compressed very slowly by dropping grains of sand onto a frictionless piston as shown in the figure…..serway. As each grain lands on the piston and compresses the gas a small amount, the system dervaites from an equilibrium state, but the differences between states are so small that the entire process can be approximated as occurring through continually

equilibrium states. The processs can be reversed by slowly removing grains from the piston.

Think about this:

During the compression process, the gas loses energy in the form of heat to maintain a constant temperature. Doesn't that violate the second law since there is a decrease in entropy? How much do you think is the overall change in entropy during this process (compression)?

(Hint: Think of the overall system)

For a reversible process the overall change in entropy is zero. (if a process causes an increase in entropy, then the reverse process couldn't happen). Therefore, a reversible heat engine has the maximum possible efficiency allowed by the second law of thermodynamics.

1.5 Heat engines and refrigerator

As defined earlier, a heat engine is a device that transforms heat energy into mechanical work. It takes in energy by heat and, operating in a cyclic process, expels a fraction of that energy by means of work. For instance, in a typical process by which a power plant produces electricity, a fuel such as coal is burned and the high-temperature gases produced are used to convert liquid water steam. This steam is directed at the blades of a turbine, setting it into rotation. The mechanical energy associated with this rotation is used to drive an electric generator. Another device that can be modeled as a heat engine is the internal combustion engine in an automobile. This device uses energy from a burning fuel to perform work on pistons that result in the motion of the automobile.

All heat engines require temperature gradient to function. At the heart of every engine is a working substance. The key events in a heat engine are:

- The working substance absorbs energy from a high-temperature heat source
- Work is done by the engine(using part of the energy absorbed)
- Energy is expelled by heat to a low temperature heat sink (cold sink)

It could be water or a gas running through the engine undergoing different thermodynamic process to complete a cycle.

The first law of thermodynamics is applied to analyze the different thermodynamic processes in the heat engine. The second law sets limits on the maximum theoretical efficiency of any heat engine.

How do heat engines work?

Now we will see how heat engines with a gas working substance work using some examples. Before we dive in, it is important to remember some basic thermodynamic processes and what their PV diagram looks like.

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Quick quiz:

1. For which isochoric process is the temperature of the gas increased?
2. Can you explain why an adiabatic expansion always end up lower than an isothermal expansion starting from the same state? on the PV graph (c) or (d)?

Efficiency of a heat engine

We know that efficiency is defined as the ration of output work to input energy. i.e.
efficiency=useful workout/total work in

In the heat engine case, the useful output work is the mechanical work done by the engine, W, and the input energy is the heat energy coming from the heat source, Qh

d...=W/Qh

but we know that Qh=W+Qc(Hence the energy coming from the heat source is partially used to do useful work partially expelled to the sink).

W=Qh-Qc … d..=Qh-Qc//Qh= 1-Qc/Qh

Example:

Internal and external combustion heat engines

Heat engines can be divided in two groups, internal and external combustion engines.

In an internal combustion engine, the working fluid consists *** of a combustion fluid placed inside a cylinder. Examples are Diesel and Petrol engines. In these engines, the fluid undergoes combustion inside the cylinder and expands. The expansion pushes a piston which is attached to a crackshaft and produces motion. There are small differences in the operating principles between peterol engines and Diesel engine: the petrol engine follows the so called Otto cycle whereas the Diesel engine follows the Diesel cycle. The Diesel engine also doesnot use a spark to produce combustion, and it is more efficient than a petrol engine.

In external combustion engine, the combustion takes place outside the piston(Remember, it is in the piston that work is done.) Steam engines are an example of external combustion engines. In steam engines, the water is boiled in a container, producing steam. The steam then expands and travels through a set of tubes, eventually arriving at the piston.

What is the maximum theoretical efficiency of a heat engine?

We have said that the second law sets limits on the maximum theoretical efficiency of any heat engine. But what is this limit?

In 1824, a French scientist and engineer named Sadi Carnot described a theoretical engine called Carnot engine. He showed that a heat engine operating in an ideal, reversible cycle- called Carnot cycle- between two energy reservoirs is the most efficient engine possible.

The maximum theoretical efficiency of a heat engine working between a hot source at temperature Th and a cold sink at temperature Tc is given by:

$$d..max = 1 - Tc/Th \text{ (remember, the temperature are in Kelvin scale)}$$

but since real process are irreversible, real engines have lower efficiencies. If a car is powered by a Carnot engine, it will have an efficiency of about 55%; an actual car's efficiency is about 25%. 100% efficiency is theoretically impossible because of the second law.

From the equation, we can see that the higher the gap between the temperatures of the heat source and the cold sink, the higher the efficiency of the engine. Since the sink is usually the environment, one usually strives to increase the efficiency by raising Th, which might create significant problems because of material expansion of the components. Thus, engine designers are continoursly researching new

materials that can withstand higher temperatures in order to increase the efficiency of future engine designs.

Refrigerators and heat pumps

Another way of stating the second law of thermodynamics is The Clausius statement of the second law of thermodynamics):

> "the spontaneous transfer of energy from a cooler body to a hotter body is not possible."

> OR alternatively

> "no series of process is possible whose sole result is the transfer of energy as heat from a reservoir at a given temperature to a reservoir at a higher temperature."

A refrigerator extracts energy from, for example, the food inside and transfers it to the room. The inside of the refrigerator is obviously at a lower temperature than the room. So how could this be possible in the light of the clausius statement above? Does not it violate the second law?

Air conditioners work in a similar way (ACs are used to cool a house during hot periods). They extract thermal energy from inside of the house and transfer the energy to the outside of which is relatively at a higher temperature.

A more general term that accommodates refrigerators and air conditioners is a heat pump. It can be thought of as a heat engine running in reverse. Heat pumps are possible because of an input work. Work goes into the heat pump and this allows energy to flow from a colder region to a hotter one. It does not violate the second law since the transfer is not spontaneous.

From the first law, we know that the energy given up to the hot reservoir must equal the sum of the work done and the energy taken in from the cold reservoir, i.e.

$$Qh=Win+Qc$$

How do refrigerators work?

Inside every fridge there is a network of pipes containing a special fluid. The fluid in its liquid state, is first allowed to expand and get cooler in the process. The cold gas is then pumped around the system, through the inside of the fridge. Thermal energy flows from the content of the fridge, which could be a bottle of water for

example, to the gas(which is colder than the inside of the fridge) work is then done on the gas (work input) to turn it back to liquid, increasingly the temperature of the fluid. The fluid then goes to the back of the refrigerator and transfters energy to the room since it is now at a higher temperature.

Think about this:

> What would happen to the temperature of a room if a refrigerator was left running with the door open? The temperature of the room increases! Can you tell why?