
**TAMPINES JUNIOR COLLEGE
PHYSICS LECTURE NOTES
JC1 2008**

TOPIC: THERMAL PHYSICS II

Syllabus Covered:

- The ideal gas equation
- Kinetic energy of a molecule
- Internal energy
- First law of thermodynamics

Assessment Objectives:

Candidates should be able to:

- (i) explain using a simple kinetic model for matter why
 1. melting and boiling take place without a change in temperature,
 2. the specific latent heat of vaporisation is higher than specific latent of fusion for the same substance
 3. cooling effect accompanies evaporation
- (j) recall and use the first law of thermodynamics expressed in terms of the change in internal energy, the heating of the system and the work done on the system.
- (k) recall and use the ideal gas equation $pV = nRT$, where n is the amount of gas in moles.
- (l) show an understanding of the significance of the Avogadro constant as the number of atoms in 0.012 kg of carbon-12.
- (m) use molar quantities where one mole of any substance is the amount containing a number of particles equal to the Avogadro constant.
- (n) recall and apply the relationship that the mean kinetic energy of a molecule of an ideal gas is proportional to the thermodynamic temperature to new situations or to solve related problems.

Content:

1. PHASES OF MATTER
2. EQUATION OF STATE OF AN IDEAL GAS
3. KINETIC THEORY FOR SOLIDS AND LIQUIDS
4. THERMODYNAMICS

REFERENCES:

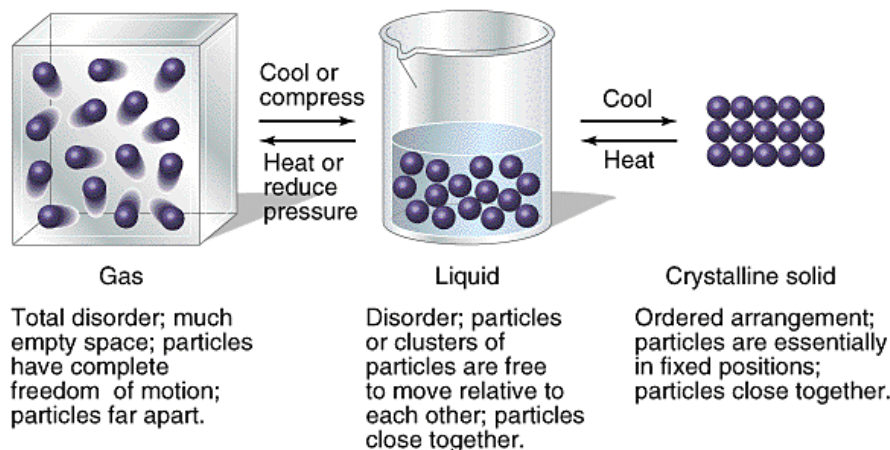
1. Tom Duncan: Physics
2. Poh LY: Pacific Physics
3. Robert Hutchings: Physics
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5. <http://itl.chem.ufl.edu>

1 PHASES OF MATTER

Matter is generally classified into four *phases*; solid, liquid, gas, and plasma, i.e. if we ignore the extreme phases like critical fluids and degenerate gases. Within each phase, there may exist numerous thermodynamic states. For example, gases (i.e. same phase) at different pressures are considered to be in different *thermodynamic states*. Throughout this set of notes, the term “state” will be used exclusively to describe the thermodynamic state of a substance and not a phase of matter.

1.1 Case Study: Solid, liquid, and gaseous phases of water

Water is made up of molecules (H_2O). At room temperature, the molecules are packed closely together, and interact weakly. They do not stick together, and are able to slide and roll past one another. This gives rise to the familiar physical properties of liquid water. Because the molecules do not form any rigid structure, water has no fixed shape and adapts to the shape of its container. And because the molecules are very close to one another, water is practically incompressible.



If we make slight changes to the physical conditions, such as lowering the temperature a little, we will observe no major changes in the properties of water. However, if we reduce the temperature below a certain point, a dramatic change occurs. The molecules suddenly align with one another to form a

rigid hexagonal structure, and water now has a definite shape. This is the solid phase of water, commonly known as ice.

Similarly, if we raise the temperature of liquid water past a certain point, it abruptly enters a gaseous phase called steam. As a vapour, the molecules are spread *much further* apart, and hence interact extremely weakly. As a result, a gas also has no fixed shape, but unlike a liquid, it is easy to compress because there is enough space for the molecules to move closer to one another. Whereas a liquid placed in a container will form a puddle at the bottom of the container, a gas will expand to fill the container uniformly. Hence its volume and pressure changes with the size of the container. This significant difference of having significantly lower density (and hence pressure) forms the basis of defining an ideal gas.

1.2 Gases - Ideal vs. Real

It is often useful to be able to predict the thermodynamic state of a gas using its properties of pressure, volume or temperature. For real gases, the derived equations are very complex. But if the gas can be maintained at extremely low density, the equations become much simpler. Such characteristics whereby the actual volume occupied by the gas molecules is insignificant compared to the volume of its container, thus resulting in negligible intermolecular forces became synonymous with an ideal gas, and eventually a much simpler *equation of state* for a gas was obtained.

2 EQUATION OF STATE OF AN IDEAL GAS

Investigation of gas characteristics lead to the famous Boyle's Law and Charles' Law. Together with the Pressure Law, a combined equation of state defining the properties of an ideal gas was created. But first, some basic concepts need to be established.

2.1 Notations

The following notations will be used in this set of lecture notes:

- p - pressure of gas
- V - volume of gas
- T - thermodynamic temperature (unit K)
- R - molar gas constant ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)
- k - Boltzmann constant ($k = 1.38 \times 10^{-23} \text{ J K}^{-1}$)
- N_A - Avogadro constant ($N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$) (alternative symbol: L)
- N - total number of molecules
- n - total number of moles ($n = N/L$)
- M - total mass of gas
- m - mass of one molecule
- M_m - molar mass

2.2 Avogadro Constant and the Mole

Avogadro constant, N_A is the number of carbon atoms found in 0.012 kg of carbon-12. This is numerically equivalent to 6.02×10^{23} atoms.

A *mole* is the amount of substance of a system which contains Avogadro constant of basic entities. Hence 1 mole of sulphuric acid H_2SO_4 would contain 12.04×10^{23} H^+ ions and 6.02×10^{23} SO_4^{2-} ions.

As such, *molar* quantities refer to physical quantities associated with 1 mole of a substance. Therefore molar volume of CO_2 means the volume occupied by 1 mole of CO_2 and so on.

Example 1

If this LT were to contain one mole of students, how many chairs would we need, assuming each student uses only one chair? How many moles of feet would there be in the LT? If every student in the LT has a mass of 60 kg, what is the molar mass of the students?

Solution

- Number of chairs needed = 6.02×10^{23}
- Number of moles of feet = 2 moles
- Molar mass of the students = $6.02 \times 10^{23} \times 60$
= $3.61 \times 10^{25} \text{ kg}$

Quick Check 1

A box contains 3 mol of oxygen (O_2), 2 mol of carbon dioxide (CO_2) and 1 mol of water vapour (H_2O).

How many oxygen atoms are there inside the box?

- A $1 N_A$ B $6 N_A$ C $11 N_A$ D $12 N_A$

Quick Check 2

Helium is a monatomic gas while nitrogen is a diatomic gas.

What is the ratio $\frac{\text{number of molecules in one mole of helium gas}}{\text{number of molecules in one mole of nitrogen gas}}$?

- A 1 B 2 C 1/2 D 1/4

2.3 The Gas Laws

The following gas laws were found experimentally:

Condition: fixed mass of gas
low pressure

Boyle's law: $p \propto V^{-1}$ (T constant)

Charles' law: $V \propto T$ (p constant)

Pressure law: $p \propto T$ (V constant)

Useful Form

$$p_1 V_1 = p_2 V_2$$

$$V_1/T_1 = V_2/T_2$$

$$p_1/T_1 = p_2/T_2$$

2.4 The Equation of State (a.k.a. the Ideal Gas Law)

Combining the above three laws gives

$$pV = nRT$$

where n = no. of moles of gas (= N/N_A)

R = molar gas constant
= $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

Useful Form

(Fixed mass)

$$p_1 V_1/T_1 = p_2 V_2/T_2$$

$$\begin{aligned} \text{Another form of the equation is } pV &= nRT \\ &= (N/N_A)RT \\ &= N(R/N_A)T \\ &= NkT \end{aligned}$$

So
$$pV = NkT$$

where N = total number of molecules

$k = R/N_A = 1.38 \times 10^{-23} \text{ J K}^{-1}$

- Boltzmann constant

Note:


1. The depicted laws are true *only for ideal gases*.
2. Practical gases do not obey the ideal gas law but approximates well at
 - low pressure
 - high temperatures

Quick Check 3

The handle of a pump is slowly pushed in halfway compressing the air inside to half of its initial volume. What happens to the pressure inside?

- A Doubled B Halved C Little changed

Quick Check 4

A deflated sealed plastic ball contains cold air as it is taken out of a freezer. 

The air inside then heats up to twice its temperature. Explain what happens to:

- (a) number of moles - doubled, halved, or little changed?
- (b) pressure - doubled, halved or little changed?
- (c) volume - doubled, halved or little changed?

Quick Check 5

A rigid well-lagged container contains air which is being heated up by a heater inside until its temperature doubles. Explain what happens to:

- (a) number of moles - doubled, halved, or little changed?
- (b) volume – doubled, halved or little changed?
- (c) pressure - doubled, halved or little changed?

Quick Check 6

A rigid metallic container contains a certain amount of air and an air pump is used to pump in another same amount of air into it. Explain what happens to:

- (a) number of moles - doubled, halved, or little changed?
- (b) volume – doubled, halved or little changed?
- (c) temperature - doubled, halved or little changed?
- (d) pressure - doubled, halved or little changed?

Quick Check 7

Which of the following is the closest to being an ideal gas?

- A Carbon dioxide gas at pressure 100 kPa and temperature 10 °C
- B Nitrogen gas at pressure 1 kPa and temperature 100 K
- C Oxygen gas at pressure 1 kPa and temperature 300 K
- D Argon gas at pressure 10 Pa and temperature 200 °C

Example 2

One mole of an ideal gas is kept in a metal cylinder at temperature of 27°C and at a pressure of 1.0×10^5 Pa. [Avogadro constant = $6.02 \times 10^{23} \text{ mol}^{-1}$]

- (a) What is the volume of the gas?

$$T = 273 + 27 = 300 \text{ K} \quad \text{*ALWAYS remember this step*}$$

$$pV = nRT \Rightarrow V = \frac{1 \times 8.31 \times 300}{(1.0 \times 10^5)}$$

$$= 2.49 \times 10^{-2} \text{ m}^3 \text{ (constant)}$$

- (b) The radius of a gas molecule is estimated to be 2×10^{-10} m.
What fraction of the volume do the gas molecules occupy?

$$r = 2 \times 10^{-10} \text{ m}$$

$$\text{Volume of a single molecule} = \frac{4}{3}\pi r^3 = 3.35 \times 10^{-29} \text{ m}^3$$

$$\text{Volume of one mole of gas} = 6.02 \times 10^{23} \times (3.35 \times 10^{-29}) = 2.02 \times 10^{-5} \text{ m}^3$$

$$\text{Fraction} = \frac{(2.02 \times 10^{-5})}{(2.49 \times 10^{-2})} = 8 \times 10^{-4}$$

- (c) Find the new pressure if the temperature in the cylinder is increased to 127°C.

$$\text{New thermodynamic temperature } T_2 = 273 + 127 = 400 \text{ K}$$

At constant volume, $p \propto T$

Therefore $p_1/T_1 = p_2/T_2$

$$p_2 = (T_2/T_1)p_1$$

$$= (400/300)(1.0 \times 10^5)$$

$$= 1.33 \times 10^5 \text{ Pa}$$

- (d) At this new temperature, some gas is released from the cylinder to bring the pressure back to 1.0×10^5 Pa. Calculate the number of moles of gas removed.

Initial condition:	Final condition:
$P_2 = 1.33 \times 10^5 \text{ Pa}$	$p_3 = 1.0 \times 10^5 \text{ Pa}$
$T_2 = 400 \text{ K}$	$T_3 = 400 \text{ K}$
$V_2 = V$	$V_3 = V$
$n_1 = 1 \text{ mole}$	$n_3 = ?$

Recall that $pV = nRT$. Since V , R and T are constants,

$$\Rightarrow \frac{p_2}{n_2} = \frac{p_3}{n_3}$$

$$\Rightarrow n_3 = \frac{p_3(n_2/p_2)}$$

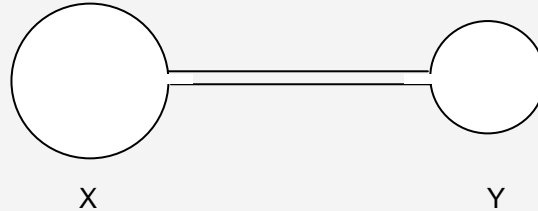
$$= \frac{(1.0 \times 10^5)(1)}{(1.33 \times 10^5)}$$

$$= 0.75 \text{ mole}$$

Hence, amount of gas removed = $1 - 0.75$
= 0.25 mole

Example 3

A vessel X of volume 200cm^3 is connected to a vessel of volume 100cm^3 by a tube of negligible volume. Both vessels contain oxygen at a pressure of $1.5 \times 10^5 \text{ Pa}$ at 300 K . The temperature of oxygen in vessel Y is increased to 500K .



- (i) What is the final pressure of the system?

Let the final pressure be p .

Note:

- The system is closed \Rightarrow Total amount of gas will be constant
i.e. $n_x + n_y = n_x' + n_y' = n$
- Vessels X and Y are linked $\Rightarrow p_x = p_y$

From note 1,

$$\begin{aligned} \frac{p_x V_x}{RT_x} + \frac{p_y V_y}{RT_y} &= \frac{p_x' V_x'}{RT_x'} + \frac{p_y' V_y'}{RT_y'} \\ \frac{1.5 \times 10^5 (200 + 100) \times 10^{-6}}{300} &= p \left(\frac{200}{300} + \frac{100}{500} \right) \\ p &= 1.73 \times 10^5 \text{ Pa} \end{aligned}$$

So the final pressure is $1.73 \times 10^5 \text{ Pa}$

- (ii) Find the number of moles of gas passing through the connecting tube.

$$\begin{aligned} n_y &= \frac{p_y V_y}{RT_y} \\ &= \frac{1.5 \times 10^5 \times 100 \times 10^{-6}}{8.31 \times 300} \\ &= 6.02 \times 10^{-3} \text{ mole} \end{aligned}$$

$$\begin{aligned} n_y' &= \frac{p_y' V_y'}{RT_y'} \\ &= \frac{1.73 \times 10^5 \times 100 \times 10^{-6}}{8.31 \times 500} \\ &= 4.16 \times 10^{-3} \text{ mole} \end{aligned}$$

$$\begin{aligned} \Delta n &= 6.02 \times 10^{-3} - 4.16 \times 10^{-3} \\ &= 1.86 \times 10^{-3} \text{ mole} \end{aligned}$$

Therefore 1.85×10^{-3} mol of gas passes through the connecting tube.

2.5 Mean K.E. of an Ideal Gas Molecule

Derivation (NOT in syllabus):

$$\text{From kinetic theory for gas,} \quad pV = (1/3)Nm\langle c^2 \rangle$$

$$\text{From ideal gas law,} \quad pV = NkT$$

$$\begin{aligned} \text{Comparing,} \quad (1/3)Nm\langle c^2 \rangle &= NkT \\ m\langle c^2 \rangle &= 3kT \end{aligned}$$

Thus the average or mean *translational* kinetic energy of a molecule is

$$\text{KE} = \frac{1}{2} m\langle c^2 \rangle = (3/2)kT$$

FAQ 1: Why use $\langle c^2 \rangle$ instead of the usual v^2 for square speed?

Ans: Different molecules in an ideal gas actually move at different speeds. The simpler 'arithmetic mean' speed does not give us the correct average kinetic energy of the gas molecules. It is the root-mean-square speed, written as $\sqrt{\langle c^2 \rangle}$, which gives us the correct average kinetic energy of the gas molecules.

Consider two objects: each of mass 1 kg, one having speed 2 m s^{-1} and the other 6 m s^{-1} .

Quantity	Object 1	Object 2
Speed	2 m s^{-1}	6 m s^{-1}
Kinetic energy	2 J	18 J

The average KE is $\frac{1}{2} (2 + 18) = 10 \text{ J}$

Their average speed is $\frac{1}{2} (2 + 6) = 4 \text{ m s}^{-1}$ but if we use this average speed to calculate the average KE, we get $\frac{1}{2} (1) (4)^2 = 8 \text{ J}$ which is not the correct average KE.

But if we use the root mean square speed, which is $\sqrt{\frac{2^2 + 6^2}{2}} = 4.47 \text{ m s}^{-1}$, and use it to calculate the average KE: $\frac{1}{2} (1) (4.47)^2$, we get 10 J which is the correct average KE of the objects.

Important Deductions (IN syllabus):

(i) *The mean translational kinetic energy of a gas molecule is proportional to T.*

If two molecules of ideal gases are at the same temperature, they have the same translational kinetic energy. Using this relation, the root-mean-square speed $\sqrt{\langle c^2 \rangle}$ of gases can be easily estimated:

$$\frac{1}{2} m\langle c^2 \rangle = (3/2)kT$$

$$\text{KE} \propto T$$

Useful Form

$$\text{KE}_1 / \text{KE}_2 = T_1 / T_2$$

- (ii) For the same type of gas, the root-mean-square speed is proportional to the square root of thermodynamic temperatures.

$$\frac{1}{2} m \langle c^2 \rangle = (3/2)kT$$

$$\sqrt{\langle c^2 \rangle} \propto \sqrt{T}$$

Useful Form

$$\langle c_1^2 \rangle / \langle c_2^2 \rangle = T_1 / T_2$$

Quick Check 8

A glass of water and a glass of alcohol (heavier molecules) have the same temperature. Which molecules (water or alcohol)

- (a) have the higher average kinetic energy (or both the same)
 (b) generally move faster (or both the same)

Quick Check 9

There is a cup half-full of hot water and an identical cup but full of cold alcohol (20% colder and the molecules 150% heavier).

Which molecules (water or alcohol or same) move with higher average kinetic energy?

Example 4

The r.m.s. speed of nitrogen molecules at 300K is 500 ms⁻¹.

- (i) What is the r.m.s. speed at 600K?
 (ii) At what temperature will the r.m.s. speed be twice the value at 300K?

(i) Using $\frac{\langle c_1^2 \rangle}{\langle c_2^2 \rangle} = T_1 / T_2$

$$\frac{\langle c_2^2 \rangle}{\langle c_1^2 \rangle} = \frac{600}{300} \left(\frac{500^2}{\langle c_2^2 \rangle} \right)$$

$$\sqrt{\langle c_2^2 \rangle} = 707 \text{ ms}^{-1}$$

(ii) Using $\frac{\langle c_1^2 \rangle}{\langle c_2^2 \rangle} = T_1 / T_2$

$$T_2 = \frac{(2/1)^2 (300)}{1} = 1200 \text{ K}$$

Example 5

Oxygen molecules in the earth's atmosphere have a root-mean-square speed of about 600ms⁻¹. If the relative molecular masses of oxygen and helium are 32 and 4 respectively, what is the r.m.s. speed of helium in the atmosphere?

Recall that $\frac{1}{2} m \langle c^2 \rangle \propto T$

$\Rightarrow \frac{m_x}{m_y} = \frac{\langle c_y^2 \rangle}{\langle c_x^2 \rangle}$ at constant temperature

$\Rightarrow \langle c_y^2 \rangle = \frac{32}{4} \times 600^2$

Hence r.m.s. speed of He = $1.7 \times 10^3 \text{ ms}^{-1}$

Example 6

- (a) The air cylinder of an diver has a volume of $9.00 \times 10^3 \text{ cm}^3$ and when the cylinder is filled, the air has a pressure of $2.10 \times 10^7 \text{ Pa}$ at 24°C . The diver is swimming in water of density $1.03 \times 10^3 \text{ kg m}^{-3}$ and temperature 24°C at a depth of 15.0 m . When the diver breathes in, the pressure of the air delivered from the cylinder to the diver is always equal to the pressure of the surrounding water. Atmospheric pressure is $1.01 \times 10^5 \text{ Pa}$.

Calculate, for the depth of 15.0 m ,

- (i) the total pressure on the diver,
 (ii) the volume of air available at this pressure from the cylinder.
- (b) The supply of air in (a) is sufficient for the diver to remain at a depth of 15.0 m for 45 minutes. Assuming that the diver always breathes at the same rate (i.e. the same volume of air is required per minute, regardless of pressure), how long would the air in the cylinder last for the diver at a depth of 35.0 m and a water temperature of 20°C ?

Solution

$$\begin{aligned} \text{(a)(i) Total pressure} &= P_{\text{atm}} + \rho gh \\ &= 1.01 \times 10^5 + (1.03 \times 10^3)(9.81)(15.0) \\ &= 2.52 \times 10^5 \text{ Pa} \end{aligned}$$

(ii) Since temperature remains constant,

$$\begin{aligned} p_1 V_1 &= p_2 V_2 \\ V_2 &= \frac{2.10 \times 10^7 \times 9.00 \times 10^3}{2.52 \times 10^5} \\ &\approx 750 \times 10^3 \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{(b) Rate of breathing} &= \frac{750 \times 10^3}{45} \\ &= 16.67 \times 10^3 \text{ cm}^3 \text{ min}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Pressure at 35m depth} &= 1.01 \times 10^5 + (1.03 \times 10^3)(9.81)(35.0) \\ &= 4.55 \times 10^5 \text{ Pa} \end{aligned}$$

$$\text{Using } \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$$\begin{aligned} \text{Volume at 35m depth} &= \frac{2.52 \times 10^5 \times 750 \times 10^3}{297} \times \frac{293}{4.55 \times 10^5} \\ &= 410 \times 10^3 \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Therefore duration in which the air can last} &= 410 \times 10^3 \div (16.67 \times 10^3) \\ &\approx 25 \text{ minutes} \end{aligned}$$

3 KINETIC THEORY FOR SOLIDS AND LIQUIDS

We know from the previous section that the molecules of matter do not all move at the same speed. Hence, at a particular temperature, the molecules would have a spread of kinetic energies. Some would have K.E. higher than the mean value while others have less. But regardless, the *mean* value is always directly related to the temperature.

3.1 Melting

In melting, there is no increase in temperature until the entire solid has melted but energy in the form of the *latent heat of fusion* is still being absorbed. The kinetic theory sees this supply of latent heat to a melting solid as enabling the molecules to just sufficiently overcome the forces between them such that the regular crystalline structure of the solid breaks down. The molecules now have the greater degree of freedom and disorder that characterise the liquid state. Whilst heat which increases the kinetic energy component of molecular internal energy causes a temperature rise ($Q=mc\Delta\theta$), the supply of latent heat ($Q=ml$) is regarded as increasing the potential energy component since it allows the molecules to move both closer together or farther apart.

3.2 Boiling

In boiling, there is also no increase in temperature even though heat, called *latent heat of vaporisation* is being supplied to it. When a liquid vaporises, a large amount of energy is needed to separate the molecules and allow them to move around independently as gas molecules. In addition, some energy is required to enable the vapour to push and expand against the atmospheric pressure. The energy for both these operations is supplied by the latent heat of vaporisation and like the latent heat of fusion, it affects the potential energy of the molecules, in this case by increasing it.

3.3 Evaporation

Evaporation is the process whereby the more energetic molecules near the surface of the liquid have enough energy to break away from the bonding of neighbouring molecules and also do work against the atmosphere, effectively escaping into the air as vapour. It differs from boiling in that it occurs at all temperatures while boiling occurs at fixed temperatures (boiling points). Besides, evaporation of a liquid occurs only at its surface but boiling involves the whole volume of liquid and is characterised by the formation of bubbles (vapour) throughout the liquid.

Evaporation results in cooling. This can be explained by either one of the reasons:

Macroscopic View

Latent heat of vaporisation is required for evaporation (change of phase). This energy is supplied by the remaining unevaporated liquid. Hence temperature will drop.

Microscopic View

As the most energetic molecules escape, they carry away with them a greater share of the kinetic energies. This causes the mean kinetic energy of the molecules left behind to decrease. Hence temperature drops.

FAQ 2: Why is Specific Latent Heat of Vaporisation so much greater than that of fusion?

Ans:

1 In the melting process, molecules need only to break down the structure into less ordered arrangement of molecules (there are still bonds present; they are just weakened). In vaporisation, the bonds are completely broken. This in itself requires more energy than merely rearranging molecules, as in fusion.

2 As a solid melts into a liquid, its volume increase is relatively negligible, and very little energy is required to push back against the atmosphere. As a liquid becomes a gas, the volume increase is much more substantial, so a lot more energy is required to push back the atmosphere in order for the gas to expand.

Both factors contribute to the larger magnitude of the specific latent heat of vaporisation.

3.4 Heat Capacities Revisited

Solids and Liquids

In considering heat absorption by solids and liquids, we have neglected the energy required for expansion/contraction. This poses no real problem because volume change accompanying temperature change in solids and liquids are rather insignificant. Any energy involved will be negligible compared to the energy required for the temperature change. As such, any heat absorption by solids or liquids inevitably results in a temperature change.

In our course, the heat capacities are also assumed to be constant at all temperatures. In actual case, however, the heat capacities do fluctuate a bit.

Gases

Gases on the other hand behave very differently from solids and liquids. When heated, their volume change can be very significant and the energy involved in this expansion or contraction must be considered. Under special conditions, it is even possible for the heat absorbed to be used entirely for expansion, without any increase in temperature. The point is that heat absorption by gases need not necessarily produce a temperature rise. This will be covered in the next section on Thermodynamics.

4 THERMODYNAMICS

Thermodynamics is the study of processes in which energy is transferred as heat and as work to or from a system. In our daily life, thermodynamic processes occur all the time. The cooling of a hot drink, melting of ice, stretching of a wire and the compressing of a gas are examples of thermo-dynamic processes in which energy is added or removed from a system as heat and as work. We have invented many useful devices that are based on the laws of thermodynamics. The following are some examples.

Devices	present in	system
Petrol engine	car	air
Steam turbine	power station	steam
Jet engine	aircraft	gas
Air-conditioner	lecture theatre	fluid

In this section, we would not concern ourselves with how exactly these devices work. Rather, we will study a common law of thermodynamics that all the devices are based on. But before we proceed, we first clarify the concept of heat and of work.

Concept of Heat

We often use the term “heat” inconsistently in everyday life. In *Thermal Physics I*, we learnt that it is wrong to say that a hot body has a lot of “heat” in it. Heat is not something that resides in a body. Rather, it is the internal energy in the body that determines its temperature. Only the energy that is transferred is called heat. But once the transferred energy is inside the body, it is no longer called heat. Instead we say that there is now more internal energy inside the body.

Concept of Work

When we exert a force on a body and there is a displacement at the point of application, work is said to be done on the body. In other words, energy has been transferred from us to the body.

Work is energy transferred from one system to another by a force moving its point of application in its direction.

Note: Work is done only when the force manages to move the point of application. For example, when we exert a force on a very stiff spring and the spring does not move (ie. not compressed) at all, then no work is done.

Heat transfer vs. Work done

Figs 1 and **2** show the transfer of energy as heat, and **Figs 3** and **4** show the transfer of energy as work.

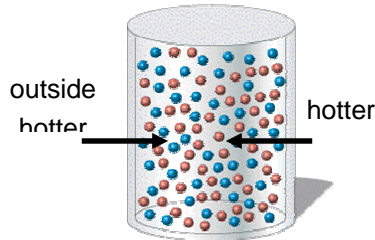


Fig. 1 Heat supplied to the gas.

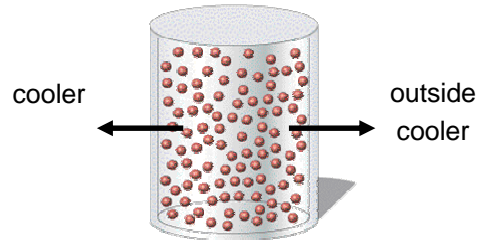


Fig. 2 Heat given off by the gas.

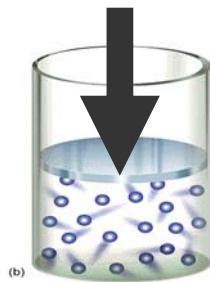


Fig. 3 Work done on the gas.

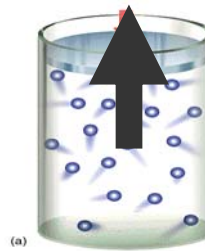


Fig. 4 Work done by the gas.

In **Fig. 1**, the surroundings being at a higher temperature supplies heat to the system. In **Fig. 2**, the surroundings is at a lower temperature and heat is given off by the system

In **Fig. 3**, the gas is compressed as the piston is pushed downwards, work is done on the gas. In **Fig. 4**, the gas expands and pushes the piston upwards, work is done by the gas.

4.1 Internal Energy in Thermodynamics

When energy is transferred as heat and as work into a system, the energy that is added to the system appears as the increase in the kinetic or potential energies of the molecules. The sum of kinetic and potential energies of the molecules is called the internal energy of the system.

Differentiating between Heat, Temperature and Internal Energy

These three terms are different. When an object of higher temperature is placed in contact with another of lower temperature, energy from the hot object is transferred to the cold object. The energy that is transferred is called heat. When energy is transferred to the cold object, the molecules of the cold object gain energy and vibrate more. There is an increase in kinetic energy of the molecules. Temperature is a measure of the *average* kinetic energy of the molecules, so an increase in the kinetic energy of the molecules means an increase in the temperature of the cold object. Internal energy is the sum of kinetic and potential energies of the molecules. Therefore the internal energy also increases. The heat transferred from the hot object to the cold object goes into the increase in the internal energy.

Tips to avoid confusion:

- *Temperature is a measure of the average kinetic energy of the individual molecules whereas internal energy is the sum of kinetic and potential energies of all the molecules.*
- *Net heat is transferred from an object of higher temperature to another of lower temperature, not from one with higher internal energy to another with lower internal energy. For instance, when a small drop of hot water is mixed with a large pool of cold water, even though the pool of cold water has greater internal energy (because it has much more molecules) than the small drop of hot water, heat is transferred from the small drop of hot water to the large pool of cold water.*
- *Heat is not the only way to change the temperature and internal energy of the system. The other way is work. This is different from what we learnt last year for solids and liquids, where heat input/output implies change in temperature ($Q = mc\Delta\theta$). This is because unlike solids and liquids, gases are highly compressible.*

4.2 First Law of Thermodynamics

Energy can be transferred as *heat* and/or as *work* into or out of a system. The internal energy of a system can be changed by the amount of heat and/or work added or removed from the system. By conservation of energy, the increase in internal energy is equal to the sum of heat and work transferred into the system. This is basically the first law of thermodynamics.

The Statement

The first law of thermodynamics states that the internal energy of a system depends only on its state; the increase in the internal energy of a system is the sum of the heat supplied to the system and the work done on the system.

The first law can be written as in the following equation:

$$\begin{array}{l} \text{increase in} \\ \text{internal energy} \\ \text{of the system} \end{array} = \begin{array}{l} \text{heat supplied} \\ \text{to the system} \end{array} + \begin{array}{l} \text{work done} \\ \text{on the system} \end{array}$$

In symbolic form, we have

$$\Delta U = q + w$$

where $\Delta U =$ *increase in the internal energy of the system,*
 $q =$ *heat supplied to the system,*
 $w =$ *work done on the system.*

Hence for the above equation, the following sign convention is used:

Sign convention for $\Delta U = q + w$

ΔU	is	positive if there is an <i>increase</i> in internal energy of the system negative if there is a <i>decrease</i> in internal energy of the system
q	is	positive if heat is <i>supplied to</i> the system negative if heat is <i>given off by</i> the system
w	is	positive if work is done <i>on</i> the system negative if work is done <i>by</i> the system

Example 7

- (a) Find the change in internal energy when 5J of heat is supplied to the system and 3J of work is done on the system.

$$\begin{aligned}\Delta U &= q + w \\ &= 5 + 3 \\ &= 8 \text{ J}\end{aligned}$$

The change in internal energy is 8 J.

- (b) 10J of heat is given off by the system while 8J of work is done on the system. What is the change in internal energy of the system?

$$\begin{aligned}\Delta U &= q + w \\ &= -10 + 8 \\ &= -2 \text{ J}\end{aligned}$$

The change in internal energy is -2 J.

- (c) The system absorbs 5J of heat while doing 7J of work. What is the loss in internal energy?

$$\begin{aligned}\Delta U &= q + w \\ &= 5 - 7 \\ &= -2 \text{ J}\end{aligned}$$

The loss in internal energy is 2 J.

- (d) The internal energy of a system increases by 10 J when 14 J of work is done on it. How much heat is lost by the system?

$$\begin{aligned}\Delta U &= q + w \\ \Rightarrow q &= \Delta U - w \\ &= 10 - 14 \\ &= -4 \text{ J}\end{aligned}$$

4J of heat is lost by the system.

- (e) A system loses 5J of heat and the internal energy decreases by 8J. How much work is done by the system?

$$\begin{aligned}\Delta U &= q + w \\ \Rightarrow w &= \Delta U - q \\ &= -8 - (-5) \\ &= -3 \text{ J}\end{aligned}$$

3 J of work is done by the system.

Example 8

The internal energy of a gas is 2000 J initially. What is its internal energy after it absorbs 400 J of heat and does 100 J of work?

$$\begin{aligned}\Delta U &= q + w \\ &= 400 - 100 \\ &= 300 \text{ J}\end{aligned}$$

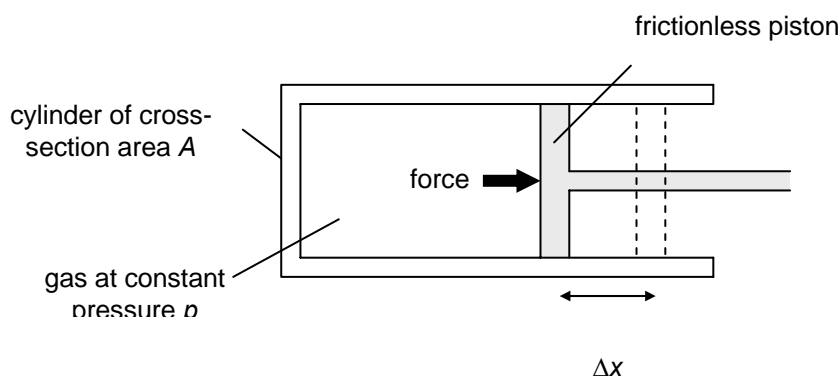
The final internal energy is $2000 + 300 = 2300 \text{ J}$.

Points to note:

- The first law of thermodynamics is really a variation of the law of conservation of energy.
- The internal energy of a system is determined *only* by the current thermodynamic state (pressure, volume, temperature, amount) of the system. It does not depend on how the system is brought to its present state. Hence we say that the internal energy is a function of state.
- The internal energy of the system is changed independently in two different ways: heating and working. Whether the internal energy increases or decreases depends on the net value of heat and work.

Work done at Constant Pressure

We can directly calculate the amount of work done on or by a system if the work is done at constant pressure. Consider a gas inside a cylinder with a frictionless piston as shown. The system in this case is the gas itself.



Suppose the gas expands and that its pressure somehow remains constant throughout the expansion. The work done by the gas at constant pressure p in displacing the piston by Δx is given by

$$\begin{aligned}\text{work done} &= \text{force} \times \text{distance} \\ &= p A \times \Delta x \\ &= p \Delta V\end{aligned}$$

$$\text{work done by a system at constant pressure} = p \Delta V$$

Note: There is work done only when the volume *changes*; if the volume *increases*, work is done *by* the system; if the volume *decreases*, work is done *on* the system. The above formula is only valid if the pressure stays constant during the change in volume.

Example 9

What is the work done by the gas in a spherical balloon of volume V when the radius is doubled at constant pressure p ?

$$\text{Since } V \propto r^3, V_{\text{new}} = 8V$$

$$\text{Hence } \Delta V = 7V$$

$$\text{Work done by gas} = 7pV$$

Example 10

At a temperature of 100°C and a pressure of $1.01 \times 10^5 \text{ Pa}$, 1.00 kg of steam occupies 1.67 m^3 but the same mass of water occupies only $1.04 \times 10^{-3} \text{ m}^3$. The specific latent heat of vaporisation of water at 100°C is $2.26 \times 10^6 \text{ J kg}^{-1}$. For a system consisting of 1.00 kg of water changing to steam at 100°C and $1.01 \times 10^5 \text{ Pa}$, find

(a) the heat supplied to the system,

$$\begin{aligned}\text{Latent heat} &= 1 \times 2.26 \times 10^6 \\ &= 2.26 \times 10^6 \text{ J}\end{aligned}$$

(b) the work done by the system,

$$\begin{aligned}\text{Work done by system} &= p \Delta V \\ &= 1.01 \times 10^5 \times (1.67 - 1.04 \times 10^{-3}) \\ &= 1.69 \times 10^5 \text{ J}\end{aligned}$$

(c) the increase in internal energy of the system.

$$\begin{aligned}\text{Increase in } U &= q + w \\ &= 2.09 \times 10^6 \text{ J}\end{aligned}$$

Example 11

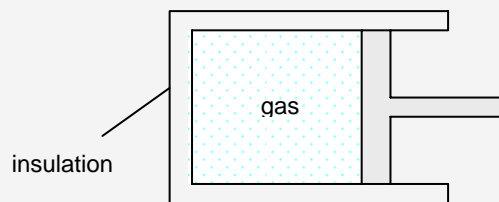
Some solids contract and some solids expand when they melt.

	Solid which contracts on melting	Solid which expands on melting
ΔU	+	+
q	+	+
w	+	-

Complete the table with the symbols + or – to indicate the signs of the thermodynamic quantities for each of the two types of solid when the solids melt at constant pressure.

Example 12

Some gas, assumed to behave ideally, is contained within a cylinder that is surrounded by insulation to prevent loss of heat, as shown in the diagram.



Initially, the volume of gas is $2.9 \times 10^{-4} \text{ m}^3$, its pressure is $1.04 \times 10^5 \text{ Pa}$ and its temperature is 314 K.

(a) Use the equation of state for an ideal gas to find the amount, in moles, of gas in the cylinder.

$$\begin{aligned}
 pV &= nRT \\
 \Rightarrow n &= pV / RT \\
 &= (1.04 \times 10^5)(2.9 \times 10^{-4}) / (8.31 \times 314) \\
 &= 0.0116 \text{ mol}
 \end{aligned}$$

(b) The gas is then compressed to a volume of $2.9 \times 10^{-5} \text{ m}^3$ and its temperature rises to 790 K. Calculate the pressure of the gas after this compression.

$$\begin{aligned}
 pV &= nRT \\
 \Rightarrow p &= nRT / V \\
 &= (0.0116)(8.31)(790) / (2.9 \times 10^{-5}) \\
 &= 2.63 \times 10^6 \text{ Pa}
 \end{aligned}$$

- (c) The work done on the gas during the compression is 91J. Use the first law of thermodynamics to find the increase in the internal energy of the gas during the compression.

As the cylinder is insulated, there is no heat flow, so $q = 0$

$$\Delta U = q + w = 0 + 91 = 91 \text{ J}$$

\therefore Increase in internal energy is 91 J

- (d) Explain the meaning of internal energy, as applied to this system, and use your result in part (c) to explain why a rise in the temperature of the gas takes place during the compression.

Internal energy is the sum of kinetic and potential energies of the molecules. For an ideal gas, potential energy is zero, the internal energy is just the total kinetic energies. From (c), there is an increase in internal energy, therefore there is an increase in the kinetic energies. Since temperature is a measure of the average kinetic energy of the molecules, an increase in kinetic energy implies a rise in the temperature of the gas.

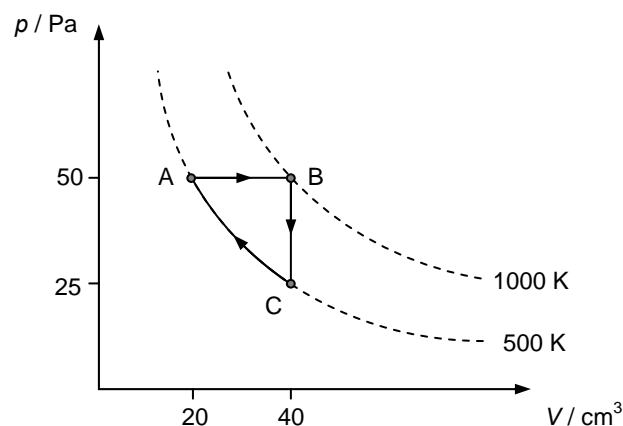
4.3 Pressure-volume Diagrams

A gas can undergo processes in which its pressure, volume and temperature change. To illustrate these changes, a graph of pressure against volume is often plotted. Such a graph is known as an *indicator diagram*.

For example, suppose a gas initially at pressure 50Pa, volume 20cm³ and temperature 500 K undergoes the following processes.

Process	Description
1	expands at constant pressure to volume 40 cm ³ and temperature 1000 K
2	cools at constant volume to temperature 500 K and pressure 25 Pa
3	contracts at constant temperature to original pressure and volume

These processes can be shown in the following p - V diagram.



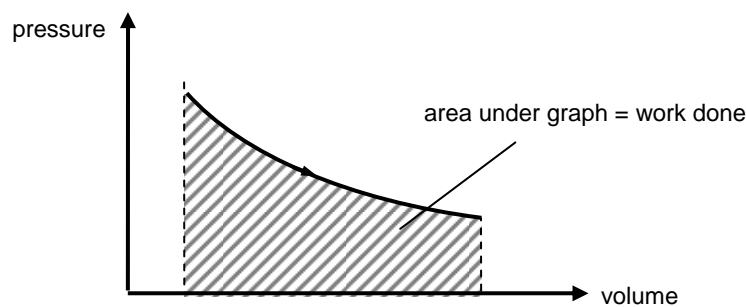
A is the starting point of the gas at pressure 50 Pa, volume 20 cm³ and temperature 500 K. Process 1 brings the gas to point B, then process 2 brings it to point C and finally process 3 brings it back to point A.

Points to note in a p - V diagram:

- The p - V diagram (or indicator diagram) is drawn for a fixed mass of gas. This implies that for an ideal gas, pV/T is constant for all points drawn on the diagram.
- The temperature T at any point is proportional to the product pV . Therefore, points with the higher value of pV have higher temperatures.
- The lines joining the points of the same temperature are called *isotherms* and have the shape of a reciprocal function: $p \propto 1/V$ for constant temperature.
- The area under the graph is equal to the *work done*. If the gas expands, then work is done *by* the gas; if the gas contracts, then work is done *on* the gas.

Work done in p - V Diagrams

As expected from the equation $W = p \Delta V$, the work done during a process can be found from the area under the p - V graph.



If the volume increases during the process, work is done *by* the system. If the volume decreases during the process, work is done *on* the system.

Various type of Processes (Optional)

A gas can undergo changes in state (pressure, volume, temperature) in many different ways. The following are some special processes.

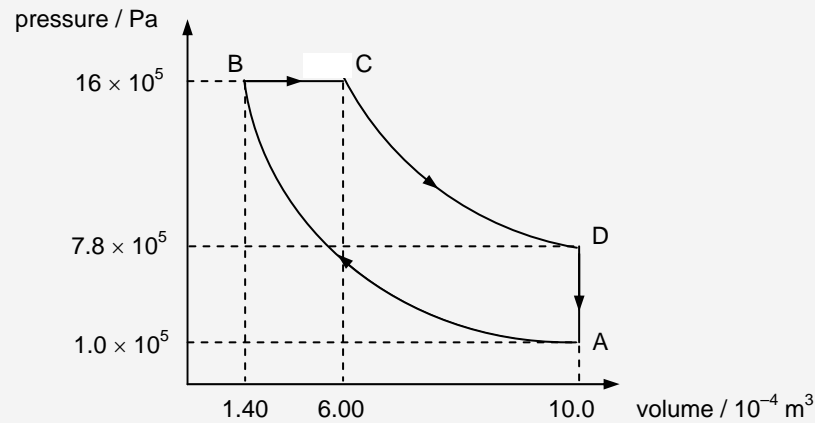
Type of process	Characteristics
<i>isochoric</i>	volume is kept constant throughout
<i>isobaric</i>	pressure is kept constant throughout
<i>isothermal</i>	temperature is kept constant throughout
<i>adiabatic</i>	no heat gain or loss throughout

Engine Cycle

In an engine, such as the car engine and the refrigerator, the system (which can be a gas or liquid) undergoes cycles of different processes repetitively. The system described in 3.3 undergoes a cycle: it starts at A, changes to B, to C and back to A again. During a cycle, the system returns to its original state. Since internal energy depends only on state, the system regains its original internal energy when it returns to its original state. The change in internal energy in a complete cycle is zero.

Example 13

The gas in the cylinder of a diesel engine can be considered to undergo a cycle of changes of pressure, volume and temperature. One such cycle, for an ideal gas, is shown on the graph.



(a) The temperatures of the gas at A and B are 300 K and 660 K respectively. Find the temperatures at C and D.

$$\frac{V_B}{T_B} = \frac{V_C}{T_C}$$

$$\Rightarrow T_C = \frac{V_C T_B}{V_B} = \frac{6.00 \times 10^{-4} \times 660}{1.40 \times 10^{-4}} = 2830 \text{ K}$$

$$\frac{p_D}{T_D} = \frac{p_A}{T_A}$$

$$\Rightarrow T_D = \frac{p_D T_A}{p_A} = \frac{7.8 \times 10^5 \times 300}{1.0 \times 10^5} = 2340 \text{ K}$$

(b) During each of the four sections of the cycle, changes are being made to the internal energy of the gas. Some of the factors affecting these changes are given in the table below.

	Heat supplied to gas / J	Work done on gas / J	Increase in internal energy of gas / J
A to B	0	300	
B to C	2580	-740	
C to D	0		
D to A	-1700		

Complete the table.

$$\text{A to B: } \Delta U = q + w = 0 + 300 = 300 \text{ J}$$

$$\text{B to C: } \Delta U = q + w = 2580 - 740 = 1840 \text{ J}$$

$$\text{D to A: } w = 0 \text{ since volume is unchanged}$$

$$\Delta U = q + w = -1700 + 0 = -1700 \text{ J}$$

ΔU in a complete cycle is zero,

$$\therefore 300 + 1840 + (\Delta U)_{C \text{ to } D} - 1700 = 0$$

$$\Rightarrow (\Delta U)_{C \text{ to } D} = -440 \text{ J}$$

C to D: $\Delta U = q + w$

$$\Rightarrow w = \Delta U - q = -440 - 0 = -440 \text{ J}$$

(c) The efficiency of a heat engine is defined as the ratio of the net work output to the heat input (exclude heat loss). Calculate the efficiency of this engine.

$$\text{efficiency} = \frac{-300 + 740 + 440}{2580} = 0.34$$

(d) Find the number of moles of the gas and use it to find the molar heat capacity of the gas at constant pressure and volume.

$$n = \frac{p_A V_A}{R T_A} = \frac{1.0 \times 10^5 \times 10 \times 10^{-4}}{8.31 \times 300} = 0.040 \text{ mol}$$

$$c_{p,m} = \frac{Q}{n \Delta T} = \frac{2580}{0.040 \times (2830 - 660)} = 29.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_{v,m} = \frac{Q}{n \Delta T} = \frac{1700}{0.040 \times (2340 - 300)} = 20.8 \text{ J mol}^{-1} \text{ K}^{-1}$$