RAFFLES INSTITUTION
YEAR 5-6 PHYSICS DEPARTMENT

Chapter 9 First Law of Thermodynamics

Content

- Kinetic Model of Matter
- Specific heat capacity
- Specific latent heat
- Internal energy
- First Law of Thermodynamics

Learning Outcomes

Candidates should be able to:

(a) define and use the concepts of specific heat capacity and specific latent heat

(b) show an understanding that internal energy is determined by the state of the system and that it can be expressed as the sum of a random distribution of kinetic and potential energies associated with the molecules of a system

(c) relate a rise in temperature of a body to an increase in its internal energy

(d) recall and use the first law of thermodynamics expressed in terms of the increase in internal energy, the heat supplied to the system and the work done on the system.

9 Introduction

Energy transfer between two substances in thermal contact usually results in temperature changes in both of them, though this is not so during a change of phase. Heat capacity and specific heat capacity allow for the calculation of temperature changes in such interactions. Similarly, latent heat is used to calculate the energy required to change the phase of a substance (e.g. from solid to liquid, or from liquid to gas).

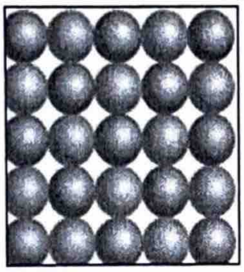
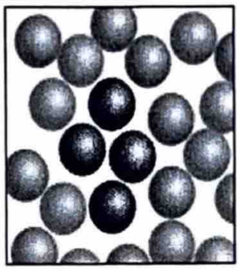
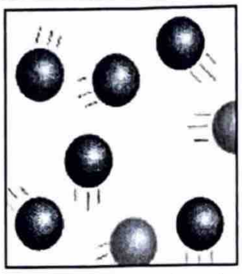
The first law of thermodynamics is central to understanding thermodynamic processes which involve heat transfer and mechanical work. This law is an extension of the conservation of energy used in mechanics as it considers energy exchange in a system by means of both heat transfer and mechanical work. The concept of internal energy is introduced to make the link between heat and mechanical work to temperature, which relates to the mechanics of atoms and molecules in a substance.

9.1 Kinetic Model of Matter

Properties of molecules in different phases

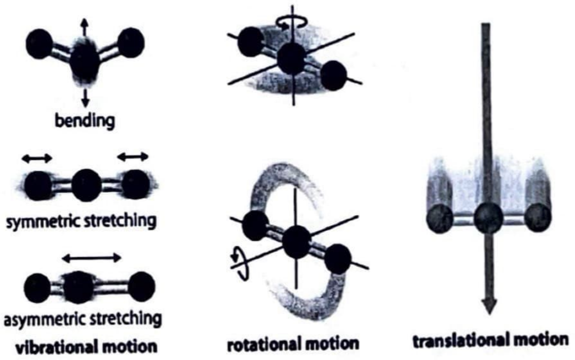
Matter is made up of a large number of molecules, which are particles whose dimensions are about 3×10^{-10} m. Evidence for the existence of molecules is given by experiments demonstrating Brownian motion (refer to Appendix in Chapter 8).

There are three phases of matter: solid, liquid and gas.

	Solid	**Liquid**	**Gas**
Packing Arrangement of Atoms/Molecules	Atoms/molecules are closely packed in a regular pattern called a lattice structure (regular, geometrical structure)	Atoms/molecules are slightly further apart than in solids	Atoms/molecules are significantly further apart
Illustration	 Crystal Lattice Structure	 Liquid atoms/ molecules	 Gas atoms/ molecules
Interatomic distance	$\approx 3\times10^{-10}$ m	$\approx 3\times10^{-10}$ m	$\sim 10^{-9}$ m
Density	High	High	Low
Volume/Shape	Fixed volume and shape	Fixed volume but takes the shape of the container	No fixed volume or shape and fills up entire space/ container in which they are placed in
Compression	Returns to their original shape when stretched or compressed (to a certain extent)	almost incompressible	easily compressed
Movement of Atoms/Molecules	Limited to vibrations of the atoms/molecules about their mean positions	Random motion throughout the liquid	Random motion at high speeds throughout the space occupied
Inter-atomic/ molecular forces	Strong intermolecular attractive and repulsive forces	Attractive cohesive forces (pulls back the molecules near the surface of the liquid, opposing their escape) No long range structure	Negligible attractive/repulsive forces between atoms/ molecules (because they are very far apart)

Microscopic Kinetic Energy

The microscopic kinetic energy (KE) of a body is due to the kinetic energies of its particles due to their constant random motion, which can be translational, rotational or vibrational.



In a body, there is a large number of particles in it (imagine how many particles a mole of a substance contains), and each particle has its own individual microscopic KE. It is usually not meaningful to consider individual particle's microscopic KE, hence we consider their average microscopic KE instead.

The temperature of a body is dependent on the average microscopic KE of all its particles (for ideal gas, temperature is **directly proportional** to the average microscopic KE). In other words, the faster the movement of a body's particles, the higher its temperature. In fact, the Kelvin scale was designed such that 0 K is the temperature at which the average microscopic KE is zero and all particles are stationary – but this is physically impossible to achieve.

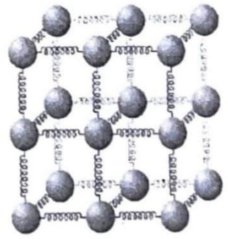
Heating a body transfers heat to the body. If it increases the microscopic KE of the body's particles, then the average microscopic KE of the body increases and hence its temperature increases.

Microscopic Potential Energy

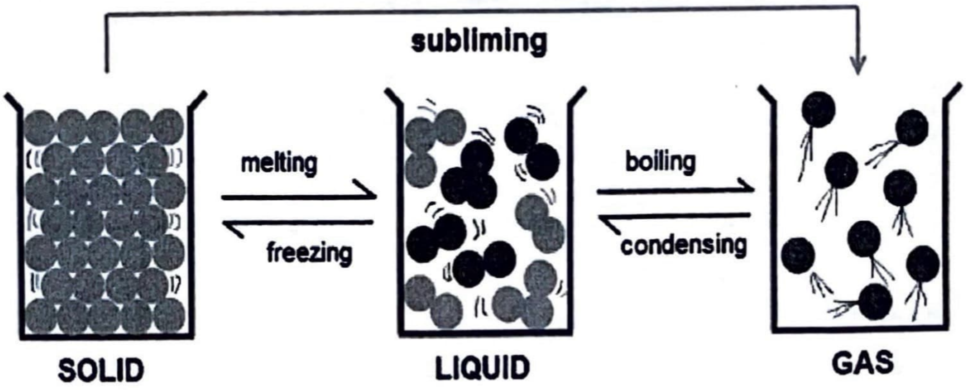
The microscopic potential energy (PE) of a body is due to the potential energies of its particles, arising from the interactions between them.

The microscopic PE of an ideal gas is defined to be zero, and since heat is required for a liquid to change into the gaseous phase, we can deduce that the microscopic PE of liquids must be lower than for gases and that microscopic PE of liquids is negative. Similarly, since heat is required for a solid to change into the liquid phase, the microscopic PE of solids is also negative and lower than that of liquids.

When a solid changes into the liquid phase, its microscopic PE is increased as the bonds are being broken. Similarly, when a liquid changes into the gaseous phase, its microscopic PE is increased as the bonds are being broken.



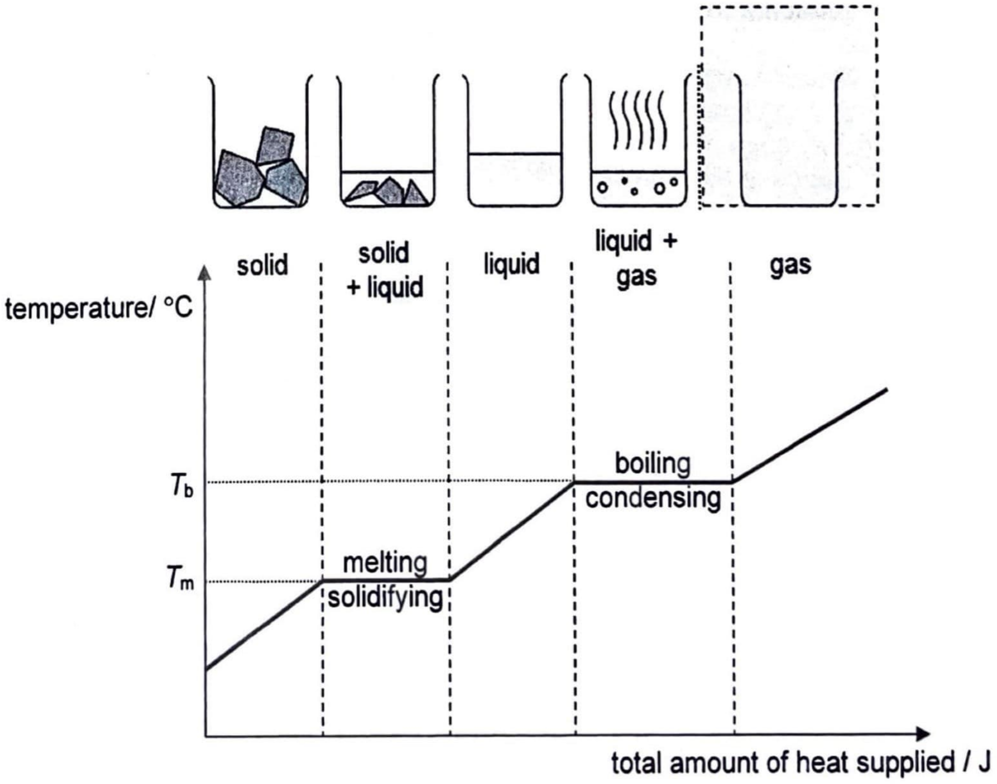
Change of Phase Heat capacity is related to changes in microscopic KE which involve changes in temperature, while latent heat is related to changes in microscopic PE which do not involve any changes in temperature, but the bonds between the particles change due to the absorption or release of heat.



Latent heat is the amount of heat required to bring about a change of phase without any change in temperature.

Latent heat of fusion	(solid → liquid)
Latent heat of vaporisation	(liquid → gas)

The transition from one phase to another is not instantaneous. During transition, the two phases coexist until the transition is completed. The figure below shows the heating curve of a substance and its phase at various temperatures.



What happens during a change in phase:

	Melting	**Boiling**
transition	Solid to liquid	Liquid to gas
inter-particle interactions	Lattice structure has to break. Some bonds are broken.	All bonds between particles have to be <u>completely</u> broken.
at melting point or boiling point	• atoms/molecules have enough microscopic KE to vibrate so violently that the attractive forces cannot hold them together • the lattice structure collapses • change of phase occurs	• heat supplied is used to overcome the attractive forces between molecules • bonds are <u>completely</u> broken • change of phase occurs
energy supplied	**Latent heat of fusion**	**Latent heat of vaporisation**
temperature	**During the process of melting and boiling, the temperature remains constant.**	

Why does melting and boiling both take place without a change in temperature?

- During melting, the heat supplied to the solid (latent heat of fusion), is used to overcome the attractive forces between the atoms or molecules which causes the lattice structure of the solid to collapse. Hence there is no increase in temperature during this phase change.
- During boiling, the heat supplied to the liquid (latent heat of vaporisation), is used to overcome the attractive forces between the molecules to break the intermolecular forces completely. Hence there is no increase in temperature during this phase change.

What are the differences between boiling and evaporation?

Both boiling and evaporation represent a change of phase from liquid to gas. Evaporation can take place at any temperature whereas boiling takes place at a fixed temperature. Evaporation takes place at the surface of the liquid whereas boiling occurs throughout the body of liquid.

Why does a cooling effect accompany evaporation?

Evaporation is the result of the exchange of energy between molecules.

- According to the kinetic theory, the molecules of the liquid are continually in motion and they make frequent collisions with each other. During collisions, some molecules gain energy while others lose energy.
- If a molecule near the surface of the liquid gains enough kinetic energy, it will be able to escape from the attractive forces of the molecules below it.
- Since the more energetic molecules escape, the average kinetic energy of the remaining molecules decreases.
- The decrease in the average microscopic kinetic energy results in a decrease in the temperature of the liquid, Thus, evaporation results in cooling.

Illustration of the cooling effect of evaporation

Consider 10 molecules in the liquid with an average kinetic energy of 1 J each.

Total kinetic energy = 10J

One energetic molecule of 2 J (remember that individual kinetic energy can vary) escapes.

New total kinetic energy = 10J - 2J = 8J

New average kinetic energy of the remaining molecules = 0.889 J

The rate of evaporation can be increased by:

(i) increasing the area of the liquid surface;

(ii) increasing the temperature of the liquid;
(increasing average microscopic kinetic energy of all the molecules);

(iii) causing a draught (wind) to remove the vapour molecules before they have a chance of returning to the liquid;

(iv) reducing the air pressure above the liquid
(decreasing probability of a vapour molecule rebounding off an air molecule).

9.2 Specific Heat Capacity

Heat Capacity The heat capacity of a body is the quantity of heat required to cause a unit rise in temperature of the body.

Mathematically, this definition can be expressed as

$$C = \frac{Q}{\Delta T}$$

where C = heat capacity
Q = quantity of heat
ΔT = change in temperature

S.I. unit: joule per kelvin (J K^{-1})

Specific Heat Capacity The specific heat capacity of a body is the quantity of heat required per unit mass to cause a unit rise in temperature of the body.

Mathematically, this definition can be expressed as

$$c = \frac{Q}{m\Delta T}$$

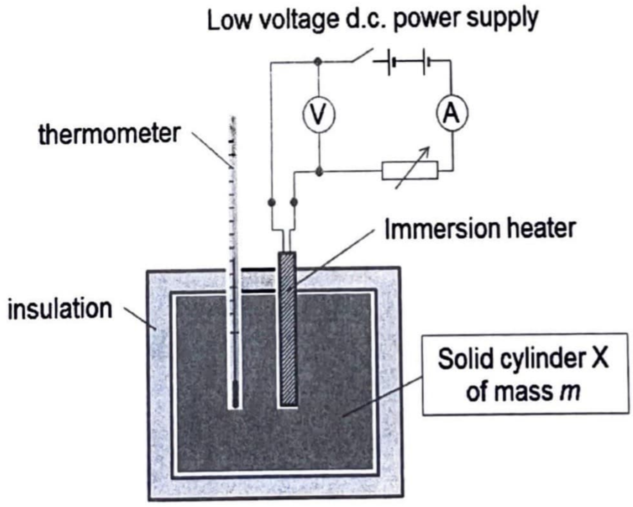
where c = specific heat capacity
Q = quantity of heat
m = mass of body
ΔT = change in temperature

S.I. unit: joule per kilogram per kelvin ($\text{J kg}^{-1}\ \text{K}^{-1}$)

Determination of Specific Heat Capacity The main principles of determining specific heat capacity by electrical methods involve heating a material through a change in temperature ΔT and comparing it to the electrical energy supplied.

Solids For *solids*, the material under test is in the form of a solid cylinder of mass m, into which two holes have been drilled to accommodate a heater and thermometer. The heater is powered by a low voltage dc supply and the variable resistor in the circuit allows potential difference and current through the heater to be varied.

Experimental Set-up



Measurements taken:

current	I
potential difference	V
time	t
mass	m
initial temperature	T_i
final temperature	T_f

Note:
In direct current (d.c.) circuits,
$P = IV$

Calculations

If *c* is the specific heat capacity of the metal, assuming negligible heat losses, by the principle of conservation of energy,

electrical energy supplied by heater = heat transferred to solid

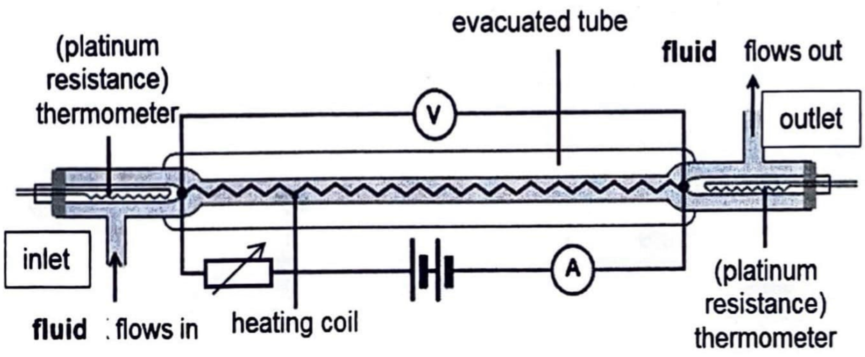
$$I\,V\,t = mc\left(T_f - T_i\right)$$

$$c = \frac{I\,V\,t}{m\left(T_f - T_i\right)}$$

Gases or Liquids For *gases* or *liquids*, the continuous flow method is used.

In this method, a steady flow of the fluid (liquid or gas), is passed along a pipe containing a heating coil. Measurements are only taken when the inlet and outlet temperatures have stabilised (i.e. the system has reached steady state). As such, the heat capacity of the apparatus can be ignored.

Experimental Set-up



Measurements taken:

current	I
potential difference	V
time	t
mass passing through in time *t*	m
inlet temperature	T_{in}
outlet temperature	T_{out}

Calculations

If *c* is the specific heat capacity of the liquid, by the principle of conservation of energy,

electrical energy supplied = heat transferred to liquid + **HEAT LOSS** (to surroundings)

$$I\,V \times t = mc\left(T_{\text{out}} - T_{\text{in}}\right) + H$$

Rearranging the above,

$$\underbrace{I\,V}_{\boxed{\text{electrical power supplied, } P}} = \underbrace{\frac{m}{t}}_{\boxed{\text{mass flow rate}}} c\left(T_{out} - T_{in}\right) + \underbrace{\frac{H}{t}}_{\boxed{\text{rate of heat loss}}} \qquad \text{....... (1)}$$

By Newton's Law of Cooling, the rate of heat loss $\frac{H}{t}$ at the inlet and outlet is proportional to the excess temperature of the apparatus, where

Excess temperature of a body = Temperature of the body − Temperature of surroundings

This means that in order to eliminate $\frac{H}{t}$, **the experiment has to be repeated with a different flow rate** and **adjusting the power of the heating coil** such that the temperatures of the fluid at the inlet and outlet remain at the same values as that of the first experiment. (Assuming temperature of surroundings remains unchanged.)

	Measurements from experiment	**Measurements from repeated experiment**
current	I	I'
potential difference	V	V'
time	t	t'
mass of liquid passing through in the given time (flow rate)	m	m'
inlet temperature	T_{in}	
outlet temperature	T_{out}	

Further Calculations

new electrical power supplied = **new** rate of heat transferred + rate of **HEAT LOSS**

$$I'V' = \frac{m'}{t'}c\left(T_{out} - T_{in}\right) + \frac{H'}{t'} \qquad \text{...... (2)}$$

Since the inlet temperature T_{in} and outlet temperature T_{out} remain unchanged, the temperature difference with the surroundings is the same, hence **the rate of heat loss at the inlet and outlet for both runs of the experiment would be the same** i.e. $\frac{H}{t} = \frac{H'}{t'}$

Solving the equations by taking (1) – (2),

$$IV - I'V' = \left(\frac{m}{t} - \frac{m'}{t'}\right)c\left(T_{out} - T_{in}\right)$$

$$c = \frac{(IV - I'V')}{\left(\frac{m}{t} - \frac{m'}{t'}\right)\left(T_{out} - T_{in}\right)}$$

Example 1 A kettle contains 700 g of water. The specific heat capacity of water is 4200 J kg^{-1} K^{-1} and the kettle itself has heat capacity 540 J K^{-1}. The kettle and its contents are heated from 15 °C to 100 °C.

(a) Calculate the heat gained by

(i) the water,

(ii) the kettle.

(b) What fraction of the total energy was used in heating the water?

(a) (i) Heat gained by water $Q_w = m_w c_w \Delta T$

$$= (0.700)(4200)(100-15)$$
$$= 249.9 \times 10^3 \text{ J}$$
$$= 250 \text{ kJ}$$

(ii) Heat gained by kettle $Q_k = C_k \Delta T$

$$= (540)(100-15)$$
$$= 45.9 \times 10^3 \text{ J}$$
$$= 45.9 \text{ kJ}$$

(b) Fraction of total energy $= \dfrac{\text{Heat gained by water}}{\text{Total heat gained by water and kettle}}$

$$= \frac{249.9}{249.9+45.9}$$
$$= 0.84$$

Example 2 A student using a continuous flow method obtains the following results:

1. Using water, which enters at 18.0 °C and leaves at 22.0 °C, the rate of flow is 20 g min^{-1}, the current in the heating element is 2.3 A and the potential difference across it is 3.3 V.
2. Using oil, which flows in and out at the same temperatures as the water, the rate of flow is 70 g min^{-1}, the current is 2.7 A and the potential difference is 3.9 V.

Taking the specific heat capacity of water to be 4200 J kg^{-1} K^{-1}, calculate

(a) the rate of heat loss from the apparatus,

(b) the specific heat capacity of oil.

By the principle of conservation of energy, considering the heating of water,

$$IV = \frac{m}{t}c\Delta T + \frac{H}{t}$$

Rate of heat loss, $\frac{H}{t} = (2.3)(3.3) - \left(\frac{0.020}{60}\right)(4200)(22-18)$

$= 1.99 \text{ J s}^{-1}$

Assuming no change in the temperature of surroundings, since the inlet and outlet temperatures are the same, the rate of heat loss for both experiments is the same.

Considering the heating of oil , by the principle of conservation of energy,

$$(2.7)(3.9) = \left(\frac{0.070}{60}\right)c_{oil}(22-18) + 1.99$$

$$c_{oil} = 1830 \text{ J kg}^{-1} \text{ K}^{-1}$$

9.3 Specific Latent Heat

Latent Heat When a solid (or liquid) is heated, its temperature rises due to the increase of the internal energy of the solid. However when the melting (or boiling) point is reached, further heating makes the solid melt (or the liquid boil) without change of temperature. This is because the heat supplied is used to rearrange the molecules of the object. Once the change of phase is completed, the temperature continues to rise if more heat is supplied.

So to change a body from the solid to the liquid phase or from the liquid to the gaseous phase, heat must be supplied to the body. Conversely, to change a liquid to its solid phase or a gas to its liquid phase, heat must be removed from the body. This amount of heat involved is called *latent heat*.

Definition

The **specific latent heat of fusion** is the quantity of heat required to convert unit mass of solid to liquid without any change of temperature.

The **specific latent heat of vaporisation** is the quantity of heat required to convert unit mass of liquid to gas without any change of temperature.

Mathematically, this definition can be expressed as

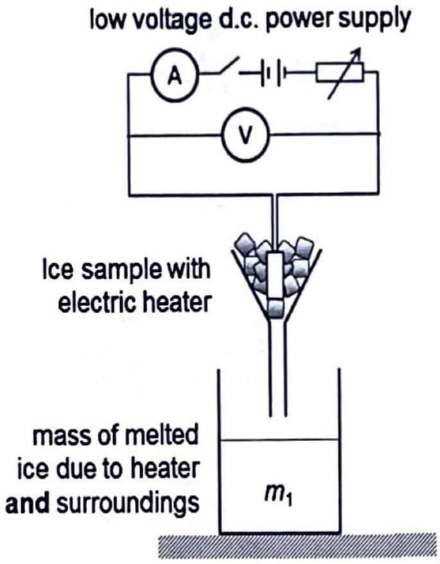
Specific latent heat of fusion:	$l_f = \dfrac{Q}{m}$	S.I. unit is joule per kilogram (J kg^{-1})
Specific latent heat of vaporisation:	$l_v = \dfrac{Q}{m}$	S.I. unit is joule per kilogram (J kg^{-1})

To determine Specific Latent Heat The main principles of determining specific latent heat by electrical methods involve heating a body through a change in phase and comparing it to the electrical energy supplied.

Latent heat of fusion A large funnel is filled with crushed ice surrounding an electric heater. Before the heater is switched on, the apparatus is left until water drips out of the funnel at a constant rate. A weighed beaker is then placed under the funnel so that the mass m of ice melted in a time duration t is determined.

The heater is then switched on and the current is kept constant. When water drips out of the funnel at a constant rate, the mass M melted in time duration t is determined.

Experimental Set-up



Measurements Taken

current	I
potential difference	V
time duration	t
mass of melted ice due to heater and surroundings in time t	M
mass of melted ice due to surroundings in time t	m

Calculations

If l_f is the specific latent heat of fusion for the solid, by the principle of conservation of energy,

$$\text{Electrical energy supplied} + \text{Heat from surroundings} = \text{Latent heat of fusion}$$

$$IV \times t + ml_f = Ml_f$$

$$IVt = (M-m)l_f$$

$$l_f = \frac{IVt}{M-m}$$

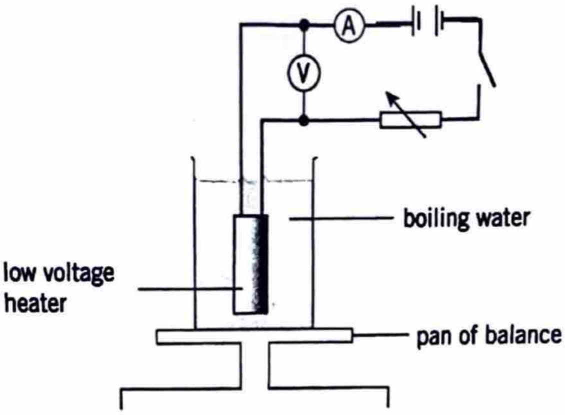
Note:

A large amount of ice should be used at the start to ensure that the heater is always surrounded by ice.

Latent heat of vaporisation

An electric heater is immersed into a beaker of liquid that is placed on the pan of a balance. The heater is switched on and the current is kept constant. When the liquid boils at a steady rate, the change in the reading m on the balance in a time duration t is determined.

Experimental Set-up



Calculations

If l_v is the specific latent heat of vaporisation of the liquid, by the principle of conservation of energy,

electrical energy supplied = latent heat of vaporisation + heat loss to surroundings

$$I\,V \times t = m l_v + H$$

Rearranging the above,

$$\underbrace{I\,V}_{\boxed{\text{electrical power supplied, } P}} = \underbrace{\frac{m}{t} l_v}_{\boxed{\text{rate of boiling}}} + \underbrace{\frac{H}{t}}_{\boxed{\text{rate of heat loss}}} \qquad \text{....... (1)}$$

As mentioned earlier, rate of heat loss $\frac{H}{t}$ is proportional to the excess temperature of the body. In this case, the excess temperature would be the difference in temperature between the boiling point of the liquid and the temperature of the surroundings.

This means that in order to eliminate $\frac{H}{t}$, **the experiment has to be repeated with a different boiling rate** by adjusting the heating power.

	Previous Measurements	**New Measurements**
current	I	I'
potential difference	V	V'
time duration	t	t'
mass of liquid collected in time t or t'	m	m'

Further Calculations

For the repeated experiment,

$$I'V' = \frac{m'}{t'} l_v + \frac{H'}{t'} \quad \ldots\ldots\ (2)$$

Since the boiling point of the liquid remains unchanged, the excess temperature of the liquid is the same. Hence **the rate of heat loss for both runs of the experiment would be the same** i.e. $\frac{H}{t} = \frac{H'}{t'}$

Solving the equations by taking (1) – (2),

$$IV - I'V' = \left(\frac{m}{t} - \frac{m'}{t'}\right) l_v$$

$$l_v = \frac{(IV - I'V')}{\left(\frac{m}{t} - \frac{m'}{t'}\right)}$$

Why is the specific latent heat of vaporisation higher than the specific latent heat of fusion for the same substance?

For example, the specific latent heat of fusion of water is 3.40×10^5 J kg^{-1} while the specific latent heat of vaporisation of water is 2.26×10^6 J kg^{-1}.

The following accounts for the difference in the two values for the same substance:

- **To melt a solid**, work must be done to separate **some** of the molecules against their mutual attractions (i.e. some molecular bonds are broken), so that the structure no longer has any rigidity. **When a liquid vaporises, all** the remaining bonds must be broken. Since melting means the breaking of relatively fewer bonds we expect the specific latent heat of fusion to be less than that of vaporisation.
- The volume occupied in the gaseous state is much larger than that in the liquid state. The gas needs to do work against the external or atmospheric pressure (boiling must be done in an open container). Energy is required by the gas to do work during the expansion process.

Example 3 An electric heater of 2.0 kW is used to heat 0.50 kg of water in a kettle of heat capacity 400 J K^{-1}. The initial water temperature is 20 °C. Neglecting heat losses,

(a) how long will it take to heat the water to its boiling point?

(b) starting from 20 °C, what mass of water is boiled away in 5.0 min?

(Specific heat capacity of water = 4200 J kg^{-1} K^{-1} and
specific latent heat of vaporisation of water = 2.0×10^6 J kg^{-1})

$$\begin{aligned} Pt &= m_{\text{water}} c_{\text{water}} \Delta T + C_{Kettle} \Delta T \\ (2000)t &= (0.50)(4200)(80) + (400)(80) \\ t &= 100 \text{ s} \end{aligned}$$

$$\begin{aligned} Pt &= m_{\text{water}} c_{\text{water}} \Delta T + C_{Kettle} \Delta T + M l_v \\ (2000)(5.0 \times 60) &= (0.50)(4200)(80) + (400)(80) + M\left(2.0 \times 10^6\right) \\ M &= 0.200 \text{ kg} \end{aligned}$$

Example 4 Ice at 0 °C is added to 200 g of water initially at 70 °C in a vacuum flask. When 50 g of ice has been added and has all melted, the temperature of the flask and contents is 40 °C. When a further 80 g of ice is added and has all melted, the temperature of the whole becomes 10 °C. Calculate the specific latent heat of fusion of ice, neglecting any heat lost to the surroundings.

The specific heat capacity of water is 4200 J kg^{-1} K^{-1}.

Heat lost by water and flask = Latent heat of fusion + Heat gained by melted ice

When 50 g of ice was initially added,

$$m_{water}c_{water}\Delta T + C_{flask}\Delta T = m_{ice}l_f + m_{ice}c_{water}\Delta T$$

$$(0.200)(4200)(30) + C_{flask}(30) = (0.050)l_f + (0.050)(4200)(40)$$

$$16800 + 30C_{flask} = 0.050l_f \text{ .... (1)}$$

When 80 g of ice was further added,

$$\boxed{m'_{water}}c_{water}\underline{\Delta T} + C_{flask}\underline{\Delta T} = \boxed{m'_{ice}}l_f + \boxed{m'_{ice}}c_{water}\Delta T'$$

$$\boxed{0.250}(4200)(30) + C_{flask}(30) = (0.080)l_f + (0.080)(4200)(10)$$

$$28140 + \underline{30C_{flask}} = 0.080\underline{l_f} \text{ .... (2)}$$

$$(0.080 - 0.050)l_f = 28140 - 16800$$

$$l_f = 378000$$

$$= 3.78 \times 10^5 \text{ J kg}^{-1}$$

9.4 Internal Energy

We have learnt that objects possess various forms of energies, of which kinetic energy (KE) and potential energy (PE) have been studied in detail in the chapter Work, Energy and Power.

In this chapter, we are more concerned with the KE and PE of the molecules in a body or system. This microscopic KE and PE tells us about the internal energy of the body or system.

Definition

The internal energy of a system is the sum of the *microscopic* kinetic energy, due to the random motion of the molecules, and the *microscopic* potential energy, associated with the intermolecular forces of the system.

Moreover, the internal energy of a system depends only on its state. This means for ideal gases it depends only on its state variables: p, V, n and T.

The KE and PE of the molecules that make up the internal energy do not include those due to the bulk movement or position of the whole body or system.

For example, the internal energy of the oxygen molecules in a cylinder of liquefied oxygen travelling on a train does not include its kinetic energy due to the net translational motion of the train or the gravitational potential energy of the train as it goes uphill.

Relationship between Temperature and Internal Energy

A rise in temperature implies an increase in the average microscopic kinetic energy of the molecules, which in turn implies an increase in the internal energy of the system, since internal energy is the sum of microscopic KE *and* microscopic PE.

For ideal gases, there is negligible intermolecular forces between the molecules. Hence, its microscopic PE is zero. This means that the internal energy of an ideal gas is only due to its microscopic KE and is therefore directly proportional to its temperature.

Internal Energy of an Ideal Gas

Recall that for a monatomic ideal gas, the microscopic kinetic energy $\langle E_K \rangle$ is directly proportional to its absolute temperature T (derivation in Chapter 8).

For **one** molecule: $\langle E_K \rangle = \frac{1}{2}m\langle c^2 \rangle = \frac{3}{2}kT$ where m is the mass of one molecule

For ***N*** molecules: $\text{total } E_K = \frac{1}{2}Nm\langle c^2 \rangle = \frac{3}{2}NkT$

The internal energy of a monatomic ideal gas is purely due to **translational** microscopic kinetic energy and is proportional to the amount of gas (N or n) and absolute temperature T only.

$$U = \text{total } E_K = \frac{3}{2}NkT$$

From the ideal gas equation, $pV = nRT = NkT$

$$\boxed{U = \frac{3}{2}NkT = \frac{3}{2}nRT = \frac{3}{2}pV}$$

The **state** of a system of an ideal gas is determined by its state variables pressure p, volume V and temperature T at that instant. Recall that the equation of state for a fixed mass of an ideal gas is given by $pV = nRT$.

Hence any change in state (and/or amount of substance n) will result in a change in internal energy ΔU.

$$\boxed{\Delta U = \frac{3}{2}Nk\Delta T = \frac{3}{2}nR\Delta T = \frac{3}{2}\Delta(pV)}$$

- ΔU is solely dependent on the change in thermodynamic temperature ΔT.
- Only a change in the product of pV which results in a change in T will result in a change in internal energy U.
- This is why the last permutation of the formula for the change in internal energy is
  $\Delta U = \frac{3}{2}\Delta(pV) = \frac{3}{2}[p_fV_f - p_iV_i]$

  * This is not the same as $\frac{3}{2}(p_f - p_i)(V_f - V_i)$, which is incorrect!

NOTE

- The factor of $\frac{3}{2}$ applies only to monatomic gases, i.e. gases made up of single atoms. Such atoms perform **translational** motion only.
- For this reason, $\frac{3}{2}kT$ is sometimes referred to as the mean **translational** kinetic energy.
- For non-monatomic molecules,
  - the molecules now have rotational and vibrational motion, in addition to the **translational** kinetic energy.
  - Hence, $\frac{3}{2}kT$ **does not apply.**
  - In this case, it is safer to analyse the ideal gas system using the First Law of Thermodynamics, which will be discussed in the next section.

Example 5 A rigid insulated container with a small opening has a volume of 5.0 m^3. It has been left in a room at a temperature of 25 °C and a pressure of 1.01×10^5 Pa. Assume that air is a monatomic ideal gas.

(a) Show that the internal energy of the air in the container is 758 kJ.

(b) The small opening is now securely connected to an air pump. 20 mol of air is pumped into the container, and the internal energy increases by 100 kJ.

Determine the new temperature of the air in the container.

a.

$$\begin{aligned}U &= \frac{3}{2}nRT\\ &= \frac{3}{2}pV\\ &= \frac{3}{2}(1.01\times10^5)(5.0)\\ &= 757\,500\,\text{J}\\ &= 758\,\text{kJ(shown)}\end{aligned}$$

b.

$$\begin{aligned}n_i &= \frac{p_iV_i}{RT_i}\\ &= \frac{(1.01\times10^5)(5.0)}{(8.31)(273.15+25)}\\ &= 203.82\,\text{mol}\end{aligned}$$

$$\begin{aligned}n_f &= n_i + 20\\ &= 203.82+20\\ &= 223.82\,\text{mol}\end{aligned}$$

$$\begin{aligned}\Delta U &= U_f - U_i\\ &= \frac{3}{2}n_fRT_f - \frac{3}{2}n_iRT_i\end{aligned}$$

$$100\,000 = \frac{3}{2}n_fRT_f - 757\,500$$

$$857\,000 = \frac{3}{2}(223.82)(8.31)T_2$$

$$\begin{aligned}T_2 &= \frac{857\,500}{\frac{3}{2}(8.31)(223.82)}\\ &= 307.35\,\text{K}\\ &= 34.2^\circ\text{C (to 3 s.f.)}\end{aligned}$$

9.5 First Law of Thermodynamics

The principle of conservation of energy states that energy can neither be created nor destroyed, but can only be transformed from one form to another.

The First Law of Thermodynamics is merely a restatement of this principle, relating work done, heat transfer and internal energy.

Consider a system of an ideal gas. If heat is supplied **to** the gas, or if work is done **on** it, the internal energy of the gas will increase.

Definition

The **First Law of Thermodynamics** states that the <u>increase</u> in the internal energy of a system is equal to the sum of the heat <u>supplied to</u> the system and the work done <u>on</u> the system, and the internal energy of a system depends only on its state.

word equation form:

INCREASE in internal energy of the system = heat **SUPPLIED TO** the system + work done **ON** the system

mathematical equation form:

$$\boxed{\Delta U = Q + W}$$

<u>Sign Conventions</u>

The First Law of Thermodynamics follows the convention as stated by its definition. Hence if any of the quantities are calculated or defined as negative, it just means the opposite of how it was defined in the First Law.

The table shows the signs of ΔU, Q and W that needs to be substituted in the equation for the first law in the different scenerios.

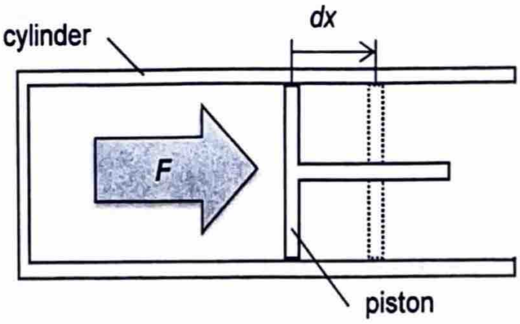
	Positive (+)	Negative (–)
ΔU	**Increase** in internal energy	**Decrease** in internal energy
Q	Heat transferred **into** the system	Heat transferred **out of** the system
W	Work done **on** the system (Compression)	Work done **by** the system (Expansion)

Heat Q Heat refers to the transfer of energy from one body to another, due to the temperature difference between the bodies. Heat is always transferred from a body with higher temperature to another body with lower temperature.

Work Done W

Consider a system of gas in a cylinder with a frictionless, movable piston of cross-sectional area A in contact with the gas. When the gas **expands**, a force F is applied on the piston **by** the gas to move the piston against the external pressure.

Using the definition of pressure, this force exerted by the gas is $F = pA$, where p is the pressure of the **gas**. Note that p is in general changing during the expansion, hence the calculation of total work done by the gas requires calculus.



The work done by this force F in displacing the piston through a small distance dx against the external pressure p is known as **positive work done by the gas**. This results in a change in volume $dV = Adx$.

Work done on the gas

$$\begin{aligned} dW &= -F\,dx \\ &= -(pA)dx = -p(A\,dx) \\ &= -p\,dV \end{aligned}$$

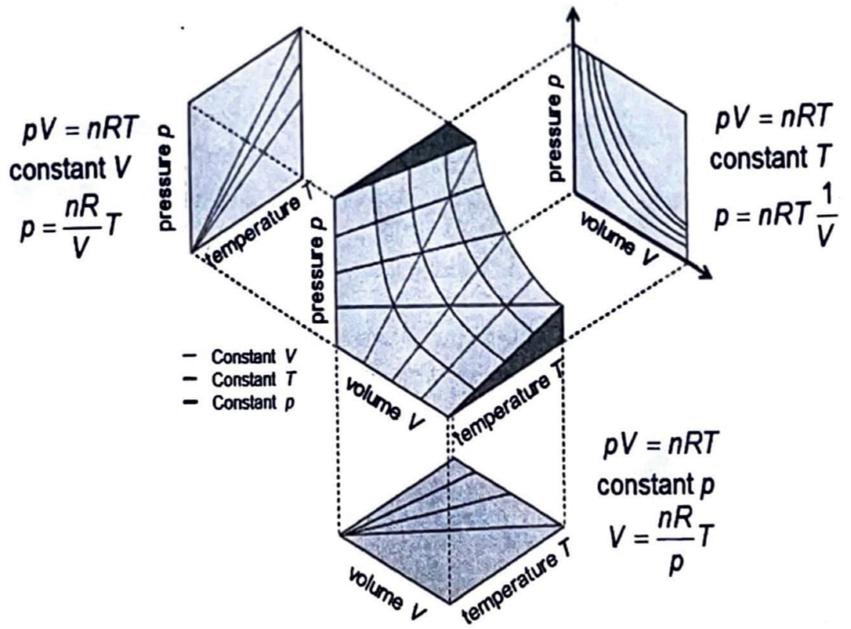
For a finite change in volume from V_i to V_f, **work done on the gas** can be inferred from the area under the pressure-volume (p-V) graph.

$$\int dW = -\int_{V_i}^{V_f} p\,dV \quad \Rightarrow W = -\int_{V_i}^{V_f} p\,dV$$

We will soon see many examples of how this is applied to p-V graphs, where both the p and V refer to the pressure and the volume of the gas.

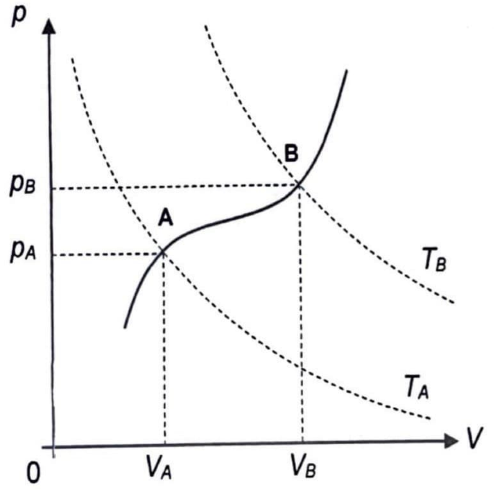
Pressure-Volume Graphs

All states of an ideal gas can be represented on a *p-V-T* surface as shown below.



For A-levels, we will largely deal with graphical representations of the relationship between pressure and volume (i.e. the *p-V* graph) as work done is determined from the area under the *p-V* graph which is a quantity we need in the first law of thermodynamics.

Information from a *p-V* graph

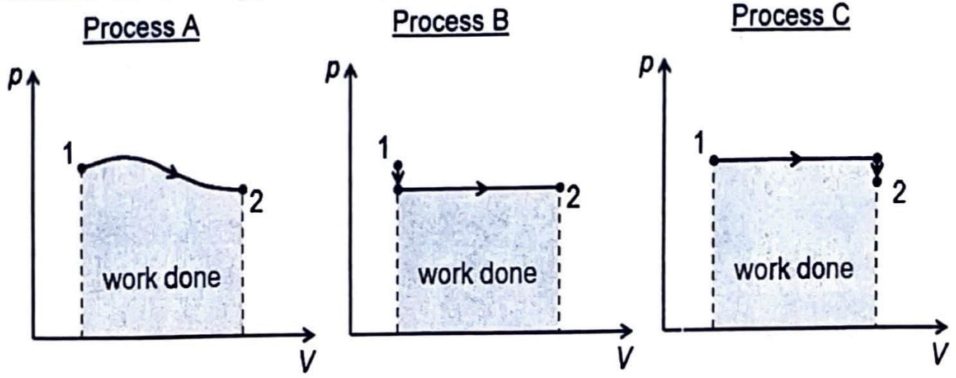


For a process from state **A** to **B**, the *p-V* graph gives us the following information:

(1) Pressure changes from p_A to p_B
(2) Volume changes from V_A to V_B
(3) This implies a temperature change from T_A to T_B
(4) Thus, there is a **change** in internal energy from U_A to U_B,
where the **increase** in internal energy is $\Delta U = U_B - U_A$

Internal Energy *U* & Work done *W*

Consider the following processes/paths from state 1 to state 2:



For a fixed mass of gas, internal energy *U* is determined by its state (i.e. *p*, *V*, *T*), which corresponds to a coordinate or position on the *p*-*V* graph.

- For all three processes A, B and C, the gas changes from state 1 to state 2.
  $\therefore \Delta U = U_2 - U_1$, is the same for all three processes.
- Work done W = area under the *p*-*V* graph
  Based on the areas shaded, $|W_B| < |W_A| < |W_C|$

In summary,

- **Internal energy *U*** is dependent only on the state of the system and the **change in internal energy Δ*U*** is hence independent of the path/process taken.
- **Work done *W***, on the other hand, is path dependent.

Special Processes

The following processes are special cases for a fixed amount of ideal gas in a cylinder with a movable piston:

(1) Isothermal Process (*T* is constant)

(2) Isobaric Process (*p* is constant)

(3) Isovolumetric / Isochoric / Isometric Process (*V* is constant)

(4) Adiabatic Process (no heat transfer, $Q = 0$)

(5) Cyclic Process

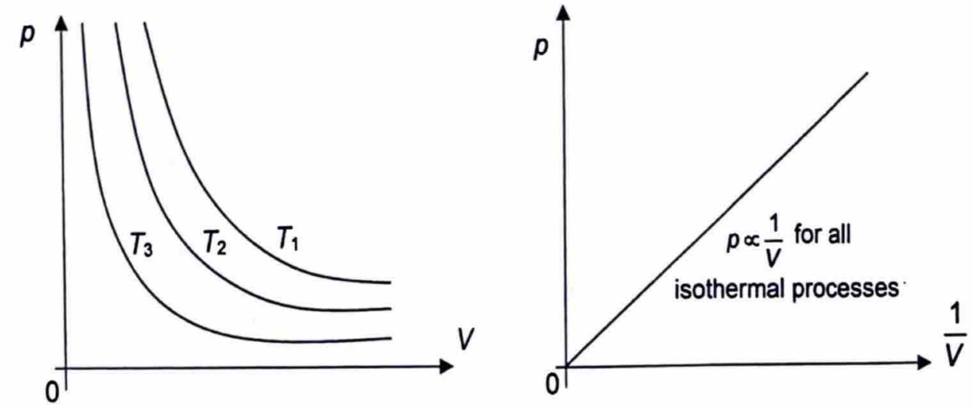
(1) **Isothermal Process** (T is constant)

Suppose the cylinder is now placed in a constant temperature water bath, and heat exchange occurs very slowly. If the change in the pressure and volume take place without a change in temperature, the process is known as an *isothermal* change.

In the p-V diagram shown, T_1, T_2 and T_3 represent isotherms. All the points on one isotherm have the same temperature.

Applying the ideal gas equation: $pV = nRT \Rightarrow p = (nRT)\frac{1}{V}$

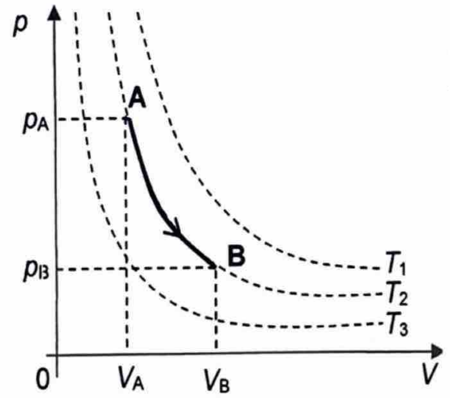
p-V diagram



At a higher temperature T, (nRT) increases, and the plot of p-V shifts upwards

- Hence, $T_1 > T_2 > T_3$
- Along each isotherm, since temperature T is constant, $\Delta U = 0$

Isothermal Expansion



In any expansion, volume increases,

- Work done **ON** the system, W is *negative*

Temperature remains the same from A to B

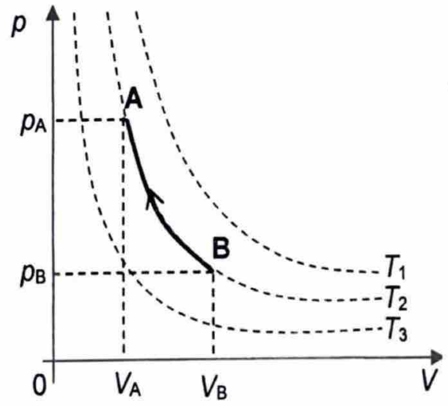
- Internal energy remains the same, $\Delta U = 0$

Process	Q	W	ΔU
A to B	+	–	0

By the 1st Law of Thermodynamics:

$$\Delta U = Q + W$$
$$Q = -W$$

Isothermal Compression



In any compression, volume decreases,

- Work done **ON** the system, W is *positive*

Temperature remains the same from B to A

- Internal energy remains the same, $\Delta U = 0$

Process	Q	W	ΔU
B to A	–	+	0

By the 1st Law of Thermodynamics:

$$\Delta U = Q + W$$
$$Q = -W$$

(2) Isobaric Process (p is constant)

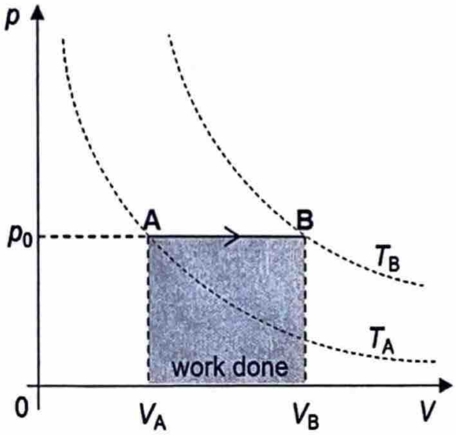
If the gas undergoes heat exchange such that its volume change occurs at constant pressure, the process is known as an *isobaric* process (*bar* is a unit of pressure). The area under the p-V graph is rectangular and the magnitude of the work done is thus $p\Delta V$.

Work done on a gas

$$W=-\int_{V_{\text{initial}}}^{V_{\text{final}}} p\,dV=-p\int_{V_{\text{initial}}}^{V_{\text{final}}} dV=-p\Delta V$$

$$\boxed{\therefore W=-p\left(V_{\text{final}}-V_{\text{initial}}\right)}$$

Isobaric Expansion



In any expansion, volume increases,

- Work done **ON** the system, W is *negative*

Temperature increases from A to B

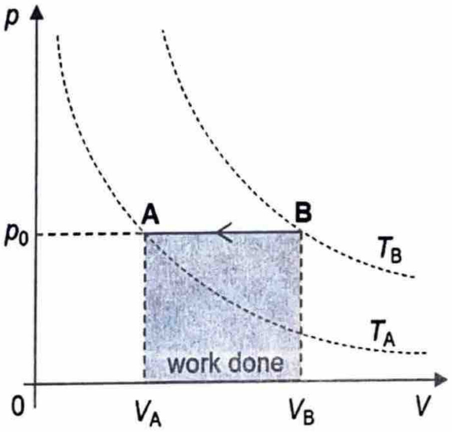
- Internal energy increases, ΔU is *positive*

Process	Q	W	ΔU
A to B	+	–	+

By the 1st Law of Thermodynamics:

$$\Delta U=Q+W$$
$$=Q-p_0\left(V_B-V_A\right)$$

Isobaric Compression



In any compression, volume increases,

- Work done **ON** the system, W is *positive*

Temperature decreases from B to A

- Internal energy decreases, ΔU is *negative*

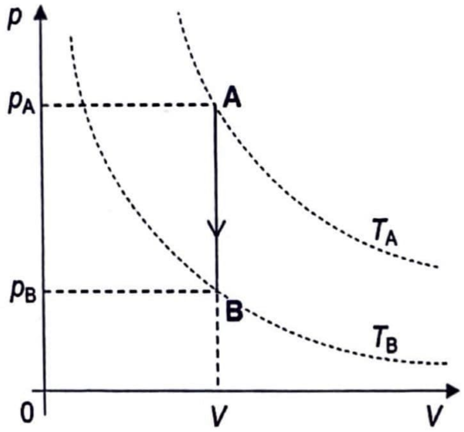
Process	Q	W	ΔU
B to A	–	+	–

By the 1st Law of Thermodynamics:

$$\Delta U=Q+W$$
$$=Q-p_0\left(V_A-V_B\right)$$

(3) Isovolumetric / Isochoric / Isometric Process (V is constant)

Suppose the piston is held in place such that the volume of the gas remains unchanged. If the change in pressure of the gas occurs without a change in volume, the process is known as an *isovolumetric* or *isochoric* or *isometric* change.



There is no change in volume

- There is no work done, $W = 0$

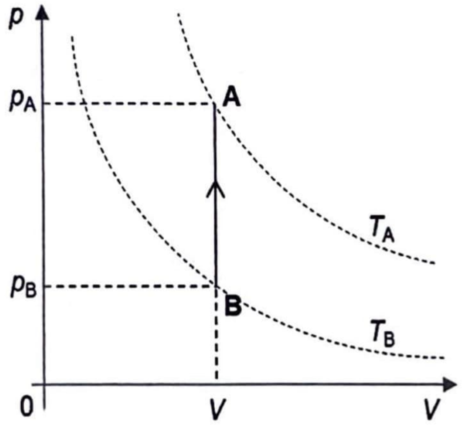
Temperature decreases from A to B

- Internal energy decreases, ΔU is *negative*

Process	Q	W	ΔU
A to B	–	0	–

By the 1st Law of Thermodynamics:

$$\Delta U = Q + W$$
$$\Delta U = Q$$



There is no change in volume

- There is no work done, $W = 0$

Temperature increases from B to A

- Internal energy decreases, ΔU is *positive*

Process	Q	W	ΔU
B to A	+	0	+

By the 1st Law of Thermodynamics:

$$\Delta U = Q + W$$
$$\Delta U = Q$$

(4) **Adiabatic Process** (no heat transfer, $Q = 0$)

When the change in pressure and volume occurs with no heat transferred into and out of the system, it is known as an *adiabatic* process.

This change in volume and pressure is accompanied by a change in temperature. (The values of all the state variables, *p*, *V* and *T* change)

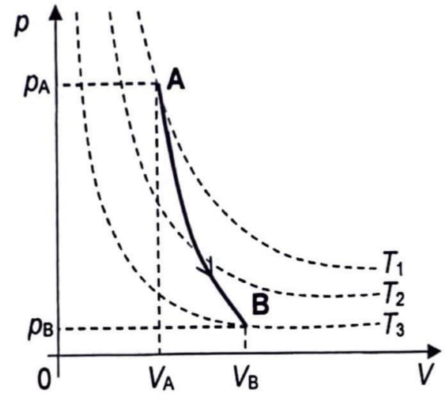
Such a process can be attained in the following cases:

(a) the system is insulated; or
(b) the change in pressure and volume occurs faster than the exchange of heat with the surroundings i.e. the process occurs rapidly.

Applying the ideal gas equation:

$$pV = nRT \Rightarrow \frac{pV}{T} = nR = \text{constant} \Rightarrow \frac{p_A V_A}{T_A} = \frac{p_B V_B}{T_B}$$

Adiabatic Expansion



There is no heat transfer

- $Q = 0$

In any expansion, volume increases,

- Work done **ON** the system, *W* is *negative*

Temperature decreases from A to B

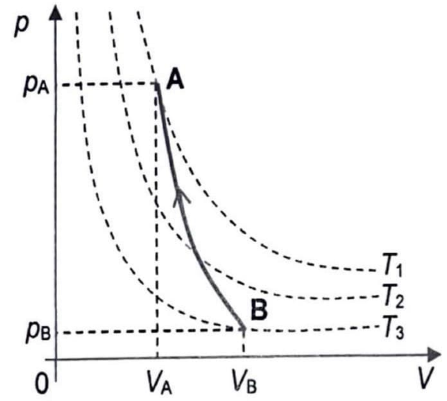
- Internal energy increases, ΔU is *negative*

Process	Q	W	ΔU
A to B	0	–	–

By the 1st Law of Thermodynamics:

$$\Delta U = Q + W$$
$$\Delta U = W$$

Adiabatic Compression



There is no heat transfer

- $Q = 0$

In any compression, volume increases,

- Work done **ON** the system, *W* is *positive*

Temperature increases from B to A

- Internal energy increases, ΔU is *positive*

Process	Q	W	ΔU
B to A	0	+	+

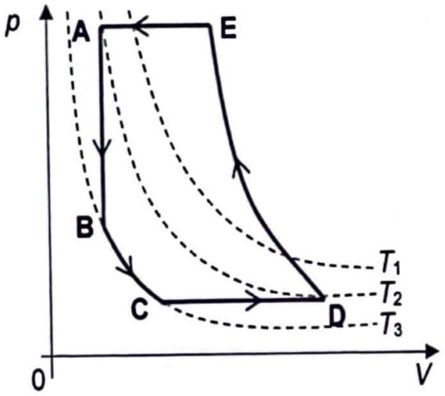
By the 1st Law of Thermodynamics:

$$\Delta U = Q + W$$
$$\Delta U = W$$

(5) Cyclic Process

A cyclic process is one in which the system goes through a series of processes and ends at its initial state.
An example of a cyclic process is shown below, where the system goes through a cycle of processes and ends up at the same initial state

anti-clockwise



Process	Q	W	ΔU
A to A	–	+	0

Internal Energy is state dependent

- cycle starts and ends at the same state
- internal energy remains the same.
- $\Delta U = 0$

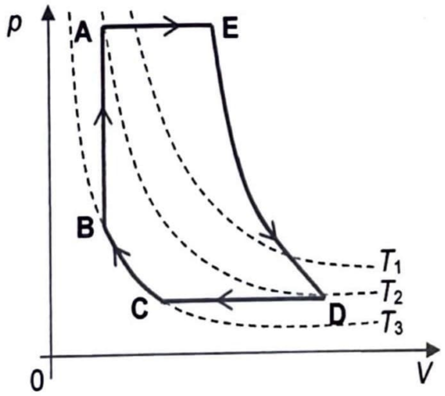
Work done is path dependent and is equal to the area under the *p*-*V* graph

- More work is done during compression (D to E to A) than during expansion (A to B to C to D)
- Net work done **ON** the system; *W* is positive.

By the 1st Law of Thermodynamics:

$$\Delta U_{\text{A to A}} = Q_{\text{A to A}} + W_{\text{A to A}}$$
$$Q_{\text{A to A}} = -W_{\text{A to A}}$$

clockwise



Process	Q	W	ΔU
A to A	+	–	0

Internal Energy is state dependent

- cycle starts and ends at the same state
- internal energy remains the same.
- $\Delta U = 0$

Work done is path dependent and is equal to the area under the *p*-*V* graph

- More work is done during expansion (A to E to D) than during compression (D to C to B to A)
- Net work done **ON** the system; *W* is negative.

By the 1st Law of Thermodynamics:

$$\Delta U_{\text{A to A}} = Q_{\text{A to A}} + W_{\text{A to A}}$$
$$Q_{\text{A to A}} = -W_{\text{A to A}}$$

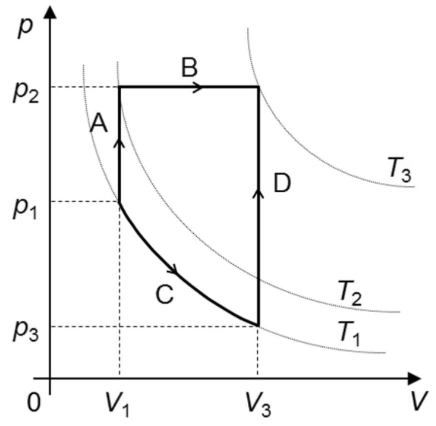
Example 6 A system of gas with pressure p_1, volume V_1, and temperature T_1 undergoes process A by being heated at constant volume to pressure p_2, volume V_1, and temperature T_2. It then undergoes an expansion by process B at constant pressure to pressure p_2, volume V_3, and temperature T_3.

An identical system undergoes an isothermal expansion by process C to pressure p_3, volume V_3, and temperature T_1. It is then heated at constant volume by process D to pressure p_2, volume V_3, and temperature T_3. So the two systems end up at the same state, characterized by the same pressure, volume and temperature.

(a) Sketch the processes described on a p-V graph.

(b) State and explain which system has more internal energy at the end.

a.



(b) Since both systems are at the same final state (this means they have the same final temperature), they will have the same internal energy at the end.

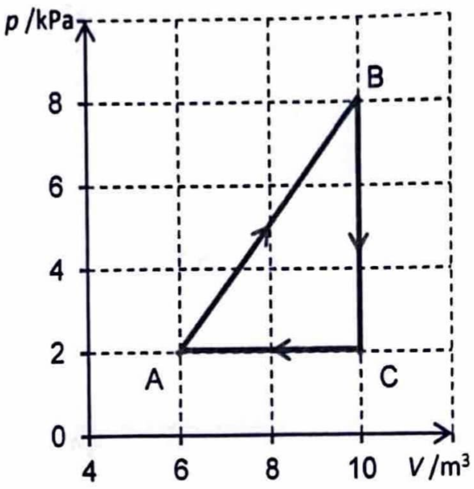
Example 7 A gas is taken through the cyclic process described in the graph below.

(a) Is there net work done on or by the gas and what is its magnitude?

(b) What is the change in the internal energy of the gas during one complete cycle?

(c) What is the net heat transferred to the gas during one complete cycle?

(d) If Q is negative for the process BC and ΔU is negative for the process CA, using the First Law of Thermodynamics, determine the signs of Q, W, and ΔU associated with each process. No calculations are required.



Process	Q	W	ΔU
A to B	+	–	+
B to C	–	0	–
C to A	–	+	–

a.

There is work done BY the gas

Work done by the gas = Area under the graph that is enclosed in the cycle

$$= \frac{1}{2}(10-6)(8-2)\times 10^3 = 12 \text{ kJ}$$

b.

Cyclic process (same initial and end state)

ΔU = 0

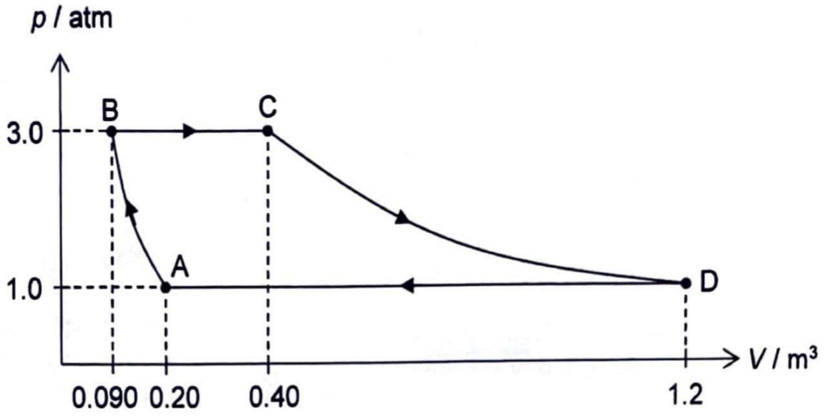
c.

$$\Delta U = Q + W$$

$$0 = Q - \left(12\times 10^3\right)$$

$$\therefore Q = 12 \text{ kJ}$$

Example 8 A sample of an ideal gas goes through the processes shown in the figure below. From A to B, the process is adiabatic; from B to C, it is isobaric with 235.5 kJ of energy entering the system. From C to D, the process is isothermal and the work done by the gas is 133.5 kJ. From D to A, the process is isobaric with 253.3 kJ of energy leaving the system.
(1 atm pressure = 1.013×10^5 Pa)



Complete the table using the information given in the question and the first law of thermodynamics.

Section of Cycle	Q	W	ΔU
A → B	0	10.7 kJ	10.7 kJ
B → C	235.5 kJ	-94.2 kJ	141.3 kJ
C → D	133.5 kJ	–133.5 kJ	0 kJ
D → A	–253.3 kJ	101.3 kJ	-152.6 kJ

Appendix

Internal Energies Of Monatomic, Diatomic And Polyatomic Gases

The internal energy of a gas is related to the number of atoms in its molecules.

A gas whose molecules consist of single atoms is said to be monatomic: for e.g. chemically inert gases and metallic vapours, Hg, Na, He, Ne, A.

A gas with two atoms in the molecule is said to be diatomic: O_2, H_2, Cl_2, CO. And a gas with more than two atoms in the molecule is said to be polyatomic: H_2O, O_3, H_2S, CO_2, CH_4. We may regard the molecules of a monatomic gas as points, but we regard those of a diatomic gas as 'dumb-bells', and those of a polyatomic gas as more complicated structures. A molecule which extends appreciably in space – a diatomic or polyatomic molecule – has an appreciable moment of inertia. It will therefore have rotational and vibrational kinetic energy, besides translational.

A monatomic molecule, however, must have a much smaller moment of inertia than a diatomic or polyatomic. Its rotational kinetic energy can therefore be neglected and thus a helium atom, for e.g. has only **translational kinetic energy**.

monatomic He   diatomic H_2 polyatomic H_2O

Phases of matter

There are more than the three phases of matter that you have learnt of, which characterises the matter's structure and properties. Another common form of matter is plasma (eg. lightning, neon lights). Other forms exist in more extreme conditions and include Bose-Einstein condensate, degenerate matter, quark-gluon plasma. Dark matter is proposed to exist in much greater proportion than our normal matter (to account for Universe's gravity), but not much of its properties are known yet due to the difficulties in observing them using light because they do not interact with it.

RAFFLES INSTITUTION
YEAR 5-6 PHYSICS DEPARTMENT

Tutorial 9 FIRST LAW OF THERMODYNAMICS

Self - Check Questions

S1 Define *specific heat capacity*, and outline the main principles of its determination for

(i) a solid, **(ii)** a liquid.

S2 Define *specific latent heat*, and outline the main principles of its determination for

(i) fusion, **(ii)** vaporisation.

S3 Explain, using the kinetic model of matter, why

(i) melting and boiling take place without a change in temperature,

(ii) the specific latent heat of vaporisation is higher than specific latent heat of fusion for the same substance,

(iii) cooling effect accompanies evaporation.

S4 Explain what is meant by the internal energy U of

(i) a system, **(ii)** an ideal gas.

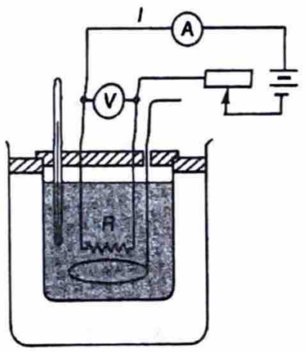
S5 State the *first law of thermodynamics* and explain how it is an application of the principle of conservation of energy.

S6 State how the internal energy of an ideal gas is related to its temperature.

S7 Explain the meaning of the terms *isobaric*, *isovolumetric*, *isothermal* and *adiabatic* when used to describe thermodynamic processes.

Self Practice Questions

SP1 The figure shows the apparatus used in the determination of the specific heat capacity of a liquid. The total heat capacity of the calorimeter, the heater, the stirrer and the thermometer was 107 J K^{-1}. The mass of liquid in the calorimeter was 0.241 kg, and the ammeter and voltmeter readings were 3.40 A and 12.2 V respectively. When the temperature of the liquid was equal to that of the surroundings, its value was found to be increasing at the rate of 46.3×10^{-3} K s^{-1}.



(a) Determine a value for the specific heat capacity of the liquid.

(b) State the advantage of measuring the rate of rise of temperature of the liquid when its temperature is equal to that of the surroundings rather than measuring the rise of temperature taking place in a given length of time.

SP2 A well-lagged copper calorimeter of mass 120 g contains 200 g of water and 50 g of ice, initially at 0 °C. Steam at 100 °C is blown through the water until the temperature reaches 30 °C. Calculate the mass of the steam that must have condensed.

Specific heat capacity of copper = 380 J kg^{-1} K^{-1}

Specific latent heat of vaporisation of water = 2.26×10^6 J kg^{-1}

SP3 A thermally insulated tube through which a gas may be passed through at constant pressure contains an electric heater and thermometers for measuring the temperature of the gas as it enters and as it leaves the tube. 3.0×10^{-3} m^3 of the gas of density 1.8 kg m^{-3} flows into the tube in 90 s and, when electrical power is supplied to the heater at a rate of 0.16 W, the temperature difference between the outlet and inlet is 2.5 K.

- **(a)** Neglecting heat loss to the surroundings, calculate the specific heat capacity of the gas at constant pressure.
- **(b)** Explain the features of the constant-flow method that makes it particularly suitable for the accurate determination of the specific heat capacities of fluids.

SP4 An ideal gas contained within a piston-cylinder assembly is compressed. 500 J of work is done and 200 J of heat is lost. Calculate the increase in the internal energy of the gas.

SP5 A 1.00 mol sample of argon gas is heated at constant pressure from 300 K to 420 K. Assuming that the gas is ideal, calculate

- **(a)** the work done on the gas,
- **(b)** the increase in its internal energy and
- **(c)** the energy transferred to the gas by heat.

SP6

- **(a)** Explain what is meant by an isothermal change.
- **(b)** How is an isothermal compression of a gas achieved in practice?
- **(c)** Explain why, in the isothermal compression of an ideal gas, the internal energy remains the same even though mechanical work is done on the system.

SP7 A cylinder fitted with a frictionless piston contains 5.0×10^{-4} m^3 of an ideal gas at a pressure of 1.0×10^5 Pa and temperature of 300 K.

The gas is then

- **(i)** heated at constant pressure to 450 K, and then
- **(ii)** cooled at constant volume to the original temperature of 300 K. The heat extracted in this stage is 37.5 J.

- **(a)** Illustrate theses changes on a *p*-*V* diagram labelled with the appropriate values of pressure and volume.
- **(b)** Determine the work done by the gas in stage **(i)**.
- **(c)** Calculate the total heat input in stage **(i)**.

SP8 An immersion heater takes time T_1 to raise the temperature of a mass M of a liquid from a temperature t_1 to its normal boiling point t_2. In a further time T_2, a mass m of the liquid is vaporised. If the specific heat capacity of the liquid is c and heat losses to the atmosphere and to the containing vessel are ignored, the specific latent heat of vaporisation is

A $\dfrac{Mc(t_2-t_1)T_2}{mT_1}$

B $\dfrac{mc(t_2-t_1)T_2}{MT_1}$

C $\dfrac{Mct_1T_2}{mT_1}$

D $\dfrac{mT_1}{Mc(t_2-t_1)T_2}$

E $\dfrac{mT_1}{Mct_1T_2}$

N77/II/29

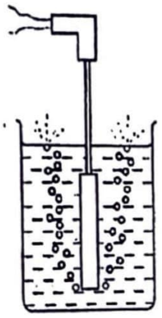
SP9 In a heating experiment, energy is supplied at a constant rate to a liquid in a beaker of negligible heat capacity. The temperature of the liquid rises at 4.0 K per minute just before it begins to boil. After 40 minutes all the liquid has boiled away.

For this liquid, what is the ratio $\dfrac{\text{specific heat capacity}}{\text{specific latent heat of vaporisation}}$?

A $\frac{1}{10}\,\text{K}^{-1}$ **B** $\frac{1}{40}\,\text{K}^{-1}$ **C** $\frac{1}{160}\,\text{K}^{-1}$ **D** $\frac{1}{640}\,\text{K}^{-1}$

J93/I/24; J2000/I/25

SP10 In an experiment to find its specific latent heat of vaporisation, water is vaporised using an immersion heater as shown.



Two sources of error in this experiment are:

error 1 water splashing out of the container;
error 2 vapour condensing on the handle of the heater and dripping back into the container.

What is the effect of these two experimental errors on the calculated value for the specific latent heat?

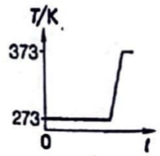
	error 1	error 2
A	decrease	decrease
B	decrease	increase
C	increase	decrease
D	increase	increase

J99/I/24

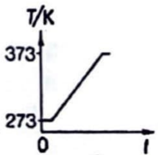
SP11 A constant power supply is used to melt 1 kg of ice, to heat the water produced, and finally to turn all the water to steam.

specific heat capacity of water $= 4 \times 10^3\ \text{J kg}^{-1}\,\text{K}^{-1}$
specific latent heat of fusion of ice $= 3 \times 10^5\ \text{J kg}^{-1}$
specific latent heat of vaporisation of water $= 2 \times 10^6\ \text{J kg}^{-1}$

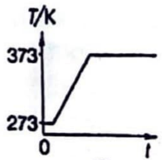
Which graph best shows how the thermodynamic temperature T varies with time t for this sequence?



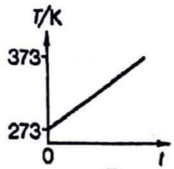
A



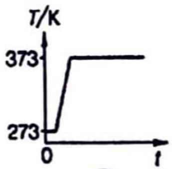
B



C



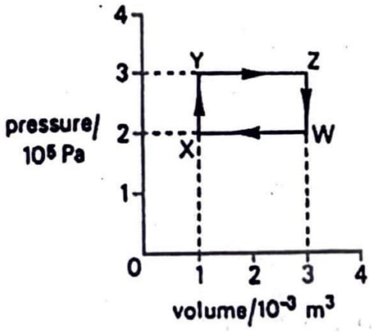
D



E

J83/II/32; J91/I/25

SP12 A gas undergoes the cycle of pressure and volume changes W→X→Y→Z→W shown in the diagram.



What is the net work done *by* the gas?

A −600 J
B −200 J
C 0 J
D 200 J
E 600 J

N89/I/3

Discussion Questions

Data:

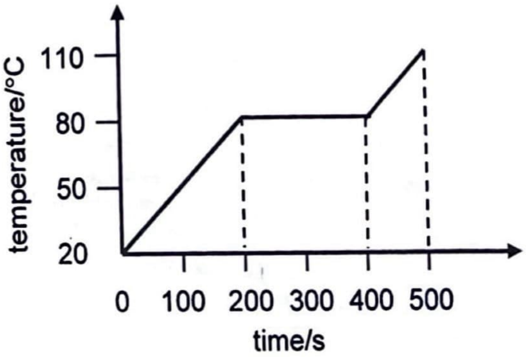
Specific heat capacity of water	4190 J kg^{-1} K^{-1}
Specific latent heat of fusion of water	3.33×10^5 J kg^{-1}
Specific latent heat of vaporisation of water	2.26×10^6 J kg^{-1}
Specific heat capacity of ice	2050 J kg^{-1} K^{-1}
Molar gas constant, R	8.31 J K^{-1} mol^{-1}
Boltzmann constant, k	1.38×10^{-23} J K^{-1}
Avogadro constant, N_A	6.02×10^{23} mol^{-1}

D1 A thermally isolated beaker contains 1.000 kg of water at 20 °C. A mass M of ice at −20 °C is dropped into it. When the system reaches thermal equilibrium, a mass m of ice remains unmelted. Show that $m = 1.123M - 0.252$, where m and M are measured in kg. (Assume that the heat transferred to the beaker is negligible.) [2]

D2 A certain solid X is heated in an insulated container at a constant rate. The temperature of the material varies as shown in the graph. If the specific heat capacity of the solid is 1800 J kg^{-1} K^{-1}, calculate

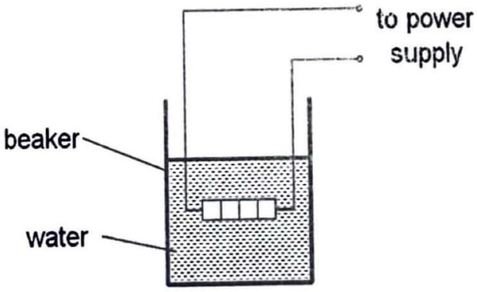
(a) the specific latent heat of fusion of the solid,

(b) the specific heat capacity of liquid X.



D3 A student carries out an experiment to determine the specific latent heat of vaporisation of water. Water is boiled in a beaker by means of an electric heater, as shown in the figure. The power supplied to the heater is measured when the water is boiling at a constant rate. The mass m of water evaporated in 5.0 minutes is determined.

Data for the power P and the mass m for two different values of P are shown.



P /W	m /g
140	14.1
95	8.2

(a) Suggest why, in order to obtain a reliable result for the specific latent heat, the mass m is determined for two different values of P. [1]

(b) Calculate the value for the specific latent heat of vaporisation. [3]

[N2010/P3/1(part)]

D4 In a space, such as a swimming pool enclosure, water at 30 °C and water vapour, also at 30 °C, coexist.

(a) Compare the pattern of movement and the speed of molecules in water and water vapour at the same temperature. [4]

(b) State what is meant by the *internal energy* of a system. [2]

(c) Using your answer in **(b)**, compare the internal energy per unit mass of water and water vapour at the same temperature. [3]

(d) Explain, in terms of internal energy, why the specific latent heat of vaporisation of a substance is greater than its specific latent heat of fusion. [2]

[N2006/P3/2(part)]

D5 **(a)** **(i)** A car tyre has a fixed internal volume of 0.0120 m^3. On a day when the temperature is 25 °C, the pressure in the tyre has to be increased from 2.62×10^5 Pa to 3.23×10^5 Pa. Assuming the air is an ideal gas, calculate the amount of air in moles which has to be supplied at constant temperature. [3]

(ii) A portable supply of air used to inflate tyres has a volume of 0.0108 m^3 and is filled with air at a pressure of 8.72×10^5 Pa. Show that at 25 °C, there is more than enough air in it to supply four tyres as in **(i)**, without the pressure falling below 3.23×10^5 Pa. [2]

(b) **(i)** Show that the internal energy of a molecule of air at a temperature of 25°C is 6.17×10^{-21} J. Assume the air behaves as an ideal gas. [2]

(ii) Hence calculate the internal energy of one mole of air at a temperature of 25 °C. [1]

(iii) Calculate the increase in the internal energy of the air in the tyre in **(a)(i)** as a result of increasing its pressure. [2]

[N2007/P3/6(part)]

D6 A mass of 5.6 g of nitrogen gas occupies a volume of 4.6×10^3 cm^3 at a pressure of 1.0×10^5 Pa and a temperature of 280 K. The specific heat capacity of nitrogen gas, when heated at constant volume, is 0.73 J g^{-1} K^{-1}. Nitrogen may be assumed to be an ideal gas.

(a) Calculate the *thermal energy* required to raise the temperature of the gas by 1 K at constant volume. [2]

(b) The temperature of the gas is raised from 280 K to 281 K at constant pressure.

Determine, for this temperature change,

(i) the change in volume of the gas, [2]

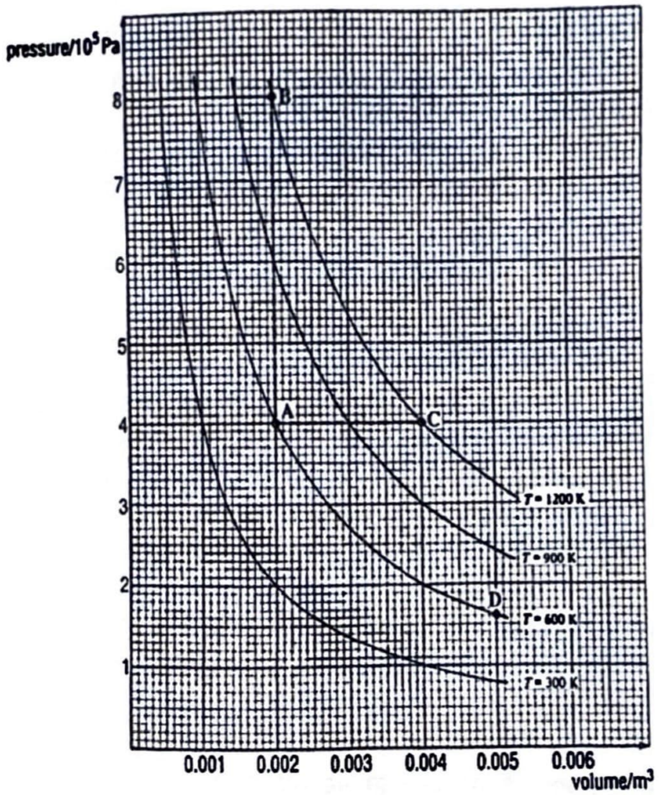
(ii) the external work done by the gas. [2]

(c) **(i)** State the first law of thermodynamics, indicating the directions of all energy changes. [2]

(ii) Use the first law and your answers in **(a)** and **(b)** to determine the *thermal energy* required to raise the temperature of the nitrogen gas from 280K to 281 K when the gas is heated at constant pressure. [1]

[N2011/P3/Q2]

D7 The figure below gives data in graphical form concerning the pressure, volume and temperature of a fixed mass of gas. On each curve, the pressure is plotted against the volume at a fixed temperature.



(a) Write down the ideal gas equation and use it to find the number of moles of gas. [3]

(b) Show that the data of the graph are consistent with the gas behaving as an ideal gas over the range of temperature from 300 K to 1200 K. [3]

(c) The gas has a heat capacity of 3.33 J K^{-1} at a constant volume and 4.66 J K^{-1} at constant pressure.

Using the values provided, calculate the quantity of heat required the take the gas

(i) from A to B along the line AB.

(ii) from A to C along the line AC. [3]

(d) The internal energy of the gas at A is 2000 J. Find the internal energy at B and at C. [3]

(e) How much work is done by the gas if an expansion at constant pressure takes place from A to C? [2]

(f) Explain why internal energy of the gas at D is also 2000 J. [2]

[J88/P2/Q10(part)]

D8 An adiabatic change is one in which no heat is supplied or extracted.

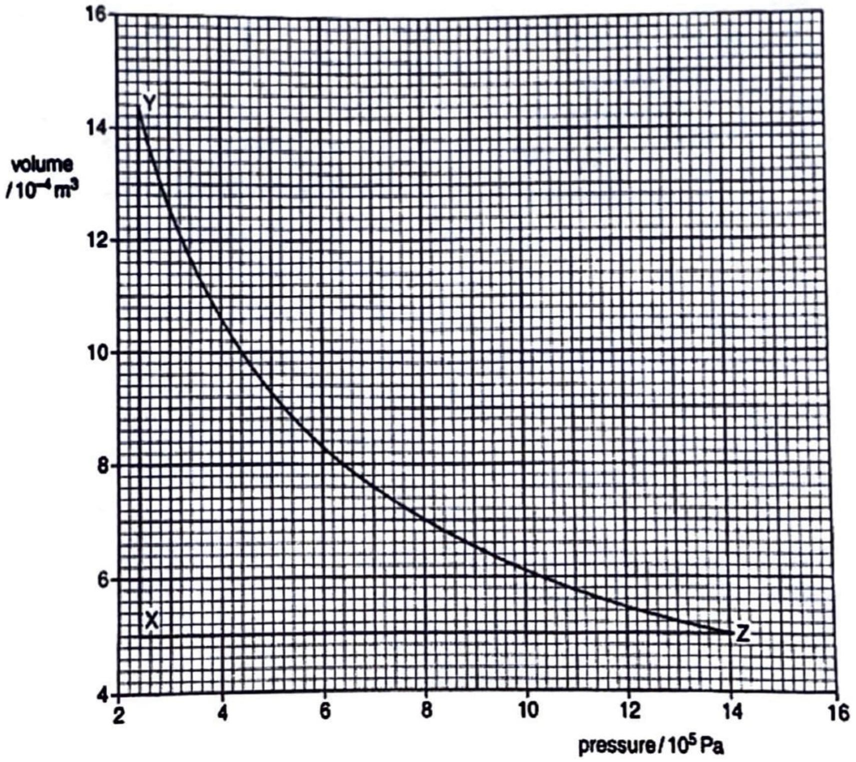
(a) Write down an expression for the first law of thermodynamics when related to an adiabatic change in the state of an ideal gas in which the gas does 600 J of work.

(b) Deduce the change in internal energy of the gas.

(c) What can you deduce about the temperature of the gas? [3]

[N89/P2/Q4]

D9 A fixed mass of an ideal gas undergoes the cycle of changes XYZX as shown in the figure.



At point X, the temperature of the gas is 290 K.

(a) Calculate the amount of gas. [2]

(b) Determine, for this mass of gas, the magnitude of

(i) the work done during the change from X to Y, [2]

(ii) the change in the internal energy during one complete cycle XYZX. [1]

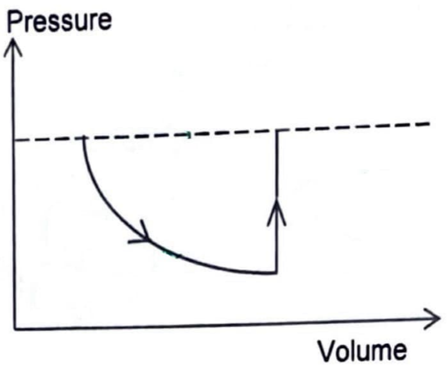
(c) Some energy changes during one cycle XYZX are shown in the following table.

change	work done on gas / J	heat supplied to gas / J	increase in internal energy / J
X → Y		+570	
Y → Z	+ 540	0	
Z → X	0		

Use your answers in **(b)** to complete the table. [3]

[N2014/P3/Q3]

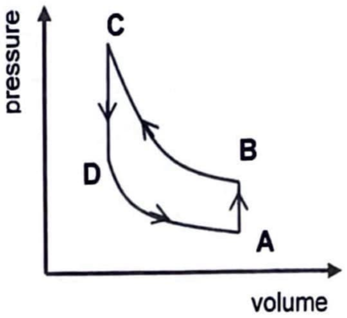
D10 **(a)** A sample of an ideal gas initially having internal energy U_1 is allowed to expand adiabatically by doing external work W. Heat Q is then supplied to it, keeping the volume constant at its new value, until the pressure rises to its original value. The internal energy is then U_2. Determine the total increase in internal energy in terms of Q and W.



[2]

(b) An ideal gas undergoes the following cyclic process ABCDA as shown. Use the first law of thermodynamics to complete the following table.

Process	Q /J	W /J	ΔU /J
AB	280		
BC	20	170	
CD	– 400		
DA		– 70	



[4]

Challenging Questions

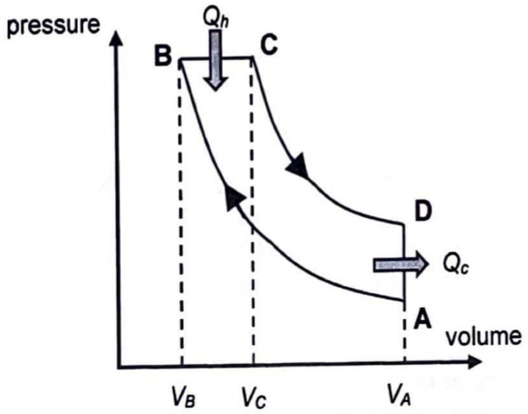
C1 A multicylinder gasoline engine in an airplane, operating at 2500 rev min^{-1}, takes in energy 7.89×10^3 J and exhaust 4.58×10^3 J for each revolution of the crankshaft.

(a) How many litres (L) of fuel does it consume in 1 hour of operation if the heat of combustion is 4.03×10^7 J L^{-1}?

(b) What is the mechanical power output of the engine? Ignore friction.

(c) What power must the exhaust and cooling system transfer out of the engine?

C2 An idealised diesel engine operates in a cycle known as the air-standard diesel cycle as shown below. Fuel is sprayed into the cylinder at the point of maximum compression, B. Combustion occurs during the expansion B → C, which is modeled as an isobaric process. Processes A → B and C → D are adiabatic processes.



Show that the efficiency of an engine operating in this idealized diesel cycle is

$$e = 1 - \frac{1}{\gamma}\left(\frac{T_D - T_A}{T_C - T_B}\right)$$

Additional information given for C2:

1. The *principal molar heat capacity* of a gas at *constant pressure*, C_P, is the amount of heat needed to raise the temperature of one mole of the gas by 1 K at constant pressure.
2. The *principal molar heat capacity* of a gas at *constant volume*, C_V, is the amount of heat needed to raise the temperature of one mole of the gas by 1 K at constant volume.
3. For an adiabatic change (or process), pV^γ = constant, where $\gamma = \frac{C_P}{C_V}$
4. $C_P - C_V = R$, the ideal gas constant.
5. The efficiency of a heat engine is defined as $e = \frac{\text{net work done in 1 cycle}}{\text{heat supplied in 1 cycle}}$

Answers

D2 (a) 1.08×10^{-5} J kg^{-1} (b) 1800 J kg^{-1} K^{-1} **D3** (b) 2.3×10^{6} J kg^{-1}
D5 (a)(i) 0.295 mol ; (b)(ii) 3710 J (iii) 1090 J **D6** (a) 4.09 J ; (b)(i) 16 cm^3 (ii) 1.6 J; (c)(ii) 5.69 J
D7 (a) 0.16 mol; (c)(i) 2000 J (ii) 2800 J; (d) 4000J; (e) 800 J
D9 (a) 0.050 mol; (b)(i) 230 J (ii) 0 J; (c) –230J, +340 J, +540 J, –880 J, –880 J
D10 (b) 0 J , 280 J, 190 J, 0 J, - 400 J, 0 J, - 70 J
C1 (a) 29.4 L (b) 1.38×10^5 W (c) 1.91×10^5 W

Suggested Solutions

Self - Check Questions

S1 Refer to notes Pg 8-10 **S2** Refer to notes Pg 13-16 **S3** Refer to notes Pg 8-10

S4 **(i)** The internal energy of a system is the sum of the microscopic kinetic energy, due to the random motion of the molecules, and the microscopic potential energy, associated with the intermolecular forces of the system.

(ii) For an ideal gas, the assumption is that the molecules have negligible forces of interactions with each other. Thus, the microscopic potential energy associated with ideal gas molecules is zero. The internal energy of an ideal gas is therefore the sum of all the microscopic kinetic energies of the gas molecules.

S5 The first aw of thermodynamics states that the increase in the internal energy of a system is equal to the sum of the heat supplied to the system and the work done on the system, and the internal energy of a system depends only on its state.

The principle of conservation of energy states that energy cannot be created or destroyed, but can be changed from one form to another.

- Since the internal energy of a system is the sum of the microscopic kinetic energy and microscopic potential energy associated with the molecules of the system, it cannot increase unless there are other forms of energy entering the system.
- In a thermodynamic system, the energy that enters a system can be in the form of heat supplied and/or work done on the system. These are transformed into internal energy of the system, thereby increasing internal energy.

S6 The internal energy of a fixed amount of ideal gas is directly proportional to its temperature.

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

S7 An *isobaric* process is one where the system undergoes heat exchange such that the volume change occurs at constant pressure.

An *isovolumetric* process is one where the system undergoes heat exchange such that the pressure change occurs at constant volume.

An *isothermal* process is one where changes in pressure and volume of a system take place without any change in temperature. This can be achieved by allowing the (heat exchange) process to occur slowly in a thin-walled vessel and by surrounding the system in a constant temperature bath.

An *adiabatic* process is one where the pressure and volume of the system change without any heat exchange. This can be achieved if the process occurs rapidly and if the system is insulated.

Self Practice Questions

SP1 **(a)** In one second,

Energy supplied = Energy gained

$$IV(1) = C_{\text{apparatus}}\Delta T + m_{\text{liquid}}c_{\text{liquid}}\Delta T$$

$$c_{\text{liquid}} = \frac{IV - C_{\text{apparatus}}\Delta T}{m_{\text{liquid}}\Delta T}$$

$$= \frac{(3.40)(12.2) - (107)(46.3\times10^{-3})}{(0.241)(46.3\times10^{-3})}$$

$$= 3273.4$$

$$= 3.27\times10^{3}\text{ kg (3 s.f.)}$$

(b) When the temperature of the liquid is equal to that of the surroundings, the apparatus is neither losing nor gaining heat from the surroundings. There is no need to take into account the heat gain from or loss to the surroundings.

SP2 By the principle of conservation of energy,

Energy lost by steam = Energy gained by ice, water & calorimeter

$$m_{\text{steam}}l_v + m_{\text{steam}}c_{water}\Delta T' = m_{\text{cal}}c_{\text{cal}}\Delta T + m_{\text{water}}c_{\text{water}}\Delta T + m_{\text{ice}}l_f + m_{\text{ice}}c_{\text{water}}\Delta T$$

$$m_{\text{steam}}\left(l_v + c_{water}\Delta T'\right) = m_{\text{cal}}c_{\text{cal}}\Delta T + \left(m_{\text{water}} + m_{\text{ice}}\right)c_{\text{water}}\Delta T + m_{\text{ice}}l_f$$

$$m_{\text{steam}}\left(2.26\times10^{6} + (4190)(70)\right) = (0.120)(380)(30) + (0.250)(4190)(30) + (0.050)(333000)$$

$$m_{\text{steam}} = \frac{(1368 + 31425 + 16650)}{\left(2.26\times10^{6} + (4190)(70)\right)}$$

$$= 0.019364$$

$$= 0.0194\text{ kg}$$

SP3 **(a)** Assuming no heat loss to the surroundings,

Electrical energy supplied = heat transferred to gas

$I\,V\,t = m\,c\,(T_{out} - T_{in})$

$0.16 \times 90 = (3.0 \times 10^{-3}) \times 1.8 \times c \times (2.5)$

$c = 1070\text{ J kg}^{-1}\text{ K}^{-1}$

(b) Measurements are only taken when the inlet and outlet temperatures have stabilised (i.e. the system has reached steady state). As such, the heat capacity of the apparatus can be ignored.

The heat loss to the surroundings can be eliminated by repeating the experiment again with a different flow rate and adjusting the power of the heating coil, such that the inlet and outlet temperatures remain at the same values as that of the first experiment.

SP4 $\Delta U = Q + W = (-200) + 500 = 300$ J

SP5 **(a)** $W = -p(\Delta V) = -nR(\Delta T)$

$= -1.00(8.31)(420-300) = -997$ J

(b) $\Delta U = \frac{3}{2}nR(T_2 - T_1)$

$= \frac{3}{2}(1.00)(8.31)(420-300)$

$= 1495.8 \text{ J} \approx 1500 \text{ J}$

(c) First law of thermodynamics,

$\Delta U = Q + W$

$Q = \Delta U - W = 1495.8 - (-997.2) = 2493 = 2490 \text{ J} \quad (3sf)$

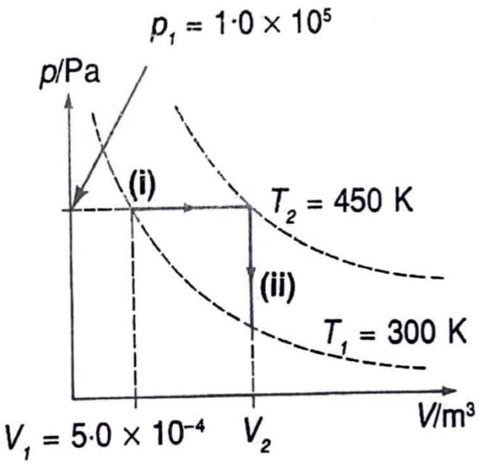
Heat energy transferred to the gas is 2490 J.

SP6 **(a)** Isothermal change refers to the change in pressure and volume of a gas under a constant temperature condition, i.e. $\Delta T = 0$.

(b) Isothermal compression of a gas can be achieved in practice by keeping the gas in a thin-walled, and good conducting vessel placed in a temperature bath. The compression is done slowly, in small steps, to allow for heat flow out of the gas to maintain a constant temperature.

(c) For isothermal compression, the rate of work done on the gas is the same as the rate at which heat is extracted from the gas; hence there is no change in the internal energy.

SP7 **(a)**



(b) $W = p_1 \Delta V = p_1(V_2 - V_1)$

Using $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ at constant p,

$V_2 = \frac{T_2}{T_1}V_1 = \frac{450}{300} \times V_1$

$W = p_1(V_2 - V_1)$

$= (1.0 \times 10^5)\left(\frac{450}{300}V_1 - V_1\right)$

$= (1.0 \times 10^5)\left(\frac{450}{300} - 1\right)(5.0 \times 10^{-4})$

$= 25$ J

(c) From stage **(ii)**, for a constant volume process, applying the first law of thermodynamics:

$\Delta U' = Q' + W' = Q' = -37.5 + 0 = -37.5$ J

Since ΔU only depends on ΔT for an ideal gas, there is no change in ΔU at the end of stage **(ii)** since the final temperature is the same as the initial temperature.

For stage **(i)**, $\Delta U = +37.5$ J

$$\Delta U = Q + W$$
$$37.5 = Q + (-25)$$
$$Q = 37.5 + 25 = 62.5 \text{ J}$$

Hence, stage **(i)** has heat input of 62.5 J.

SP8 **Answer: A**

$$Q = Mc(t_2 - t_1) \qquad \Rightarrow P = \frac{Mc(t_2 - t_1)}{T_1}$$

$$Q = ml_v \qquad \Rightarrow P = \frac{ml_v}{T_2}$$

Since power of immersion heater is constant,

$$\frac{Mc(t_2 - t_1)}{T_1} = \frac{ml_v}{T_2}$$

$$l_v = \frac{Mc(t_2 - t_1)T_2}{mT_1}$$

SP9 **Answer: D**

$$Q = mc\Delta T \qquad \Rightarrow P = mc\frac{4.0}{60}$$

$$Q = ml_v \qquad \Rightarrow P = \frac{ml_v}{40 \times 60}$$

Since energy is supplied at a constant rate, (ie power is constant)

$$mc\frac{4.0}{60} = \frac{ml_v}{40 \times 60}$$

$$\frac{c}{l_v} = \frac{1}{160}$$

SP10 **Answer: B**

Error 1

When water splashes out of the container, there is a less water left in the container. Hence, the amount of heat used to vapourize the water in the container is less than that required for the original mass. The specific latent heat of vapourisation calculated would decrease.

Error 2

When vapour condenses back into the container, there is a greater amount of water in the container. Hence, the amount of heat used to vapourise the water in the container is more than that required for the original mass. The specific latent heat of vapourisation calculated would increase.

SP11 Answer: E

Melting and vapourisation take place at constant temperature
➔ Option D is eliminated

Specific latent heat of vapourisation is larger than the specific latent heat of fusion. Hence the time taken for the vapourisation process is much longer than the melting process.
➔ Options A and B are eliminated

Specific latent heat of fusion is numerically larger than specific heat capacity. Hence, the time taken for the melting process should be comparable to the time taken for water to be heated from melting point to boiling point.
➔ Option C is eliminated

SP12 Answer: D

Net work done by the gas = area enclosed by the rectangle WXYZ
$= (1\times10^{5})\ (2\times10^{-3}) = +200$ J