RAFFLES INSTITUTION
YEAR 5-6 PHYSICS DEPARTMENT

Chapter 9 First Law of Thermodynamics

Content

- 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 causes temperature changes in both of them, though this is not guaranteed. 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 and mechanical work. This law is an extension of the conservation of energy used in mechanics as it considers energy exchange to a system by means of both heat transfer and mechanical work. The concept of internal energy is introduced to make the link between the macroscopic concepts of heat and mechanical work to the microscopic concept of temperature, which relates to the mechanics of atoms and molecules in a substance.

9.1 Specific Heat Capacity and Specific Latent Heat

Heat Capacity

Definition

The numerical value of the heat capacity of a body is the quantity of heat required to raise the temperature of the body by one degree.

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})

The unit of heat capacity is *not* the joule and this is why, in the definition of heat capacity, it is important to make reference to the *numerical value.*

Specific Heat Capacity

Definition

The numerical value of the specific heat capacity of a substance is the quantity of heat required to raise the temperature of unit mass of the substance by one degree.

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

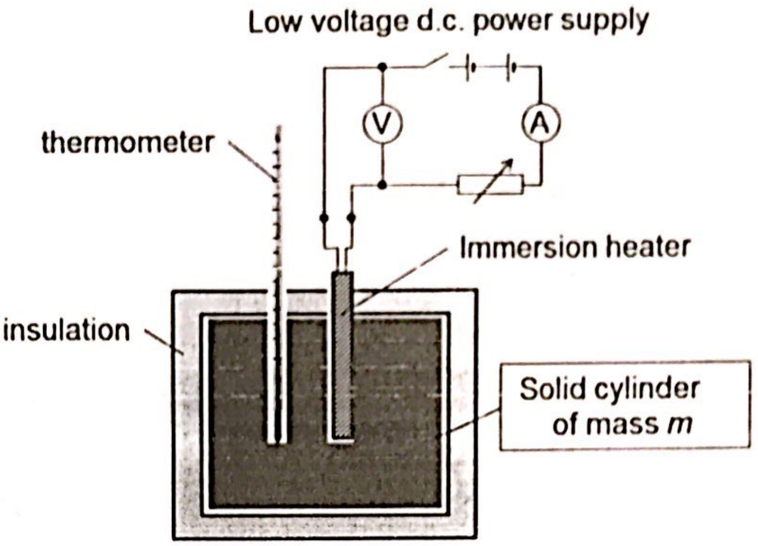
S.I. unit: joule per kilogram per kelvin ($\text{J kg}^{-1}\ \text{K}^{-1}$)

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.

Experimental Set-up



Measurements taken:

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

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 received by block

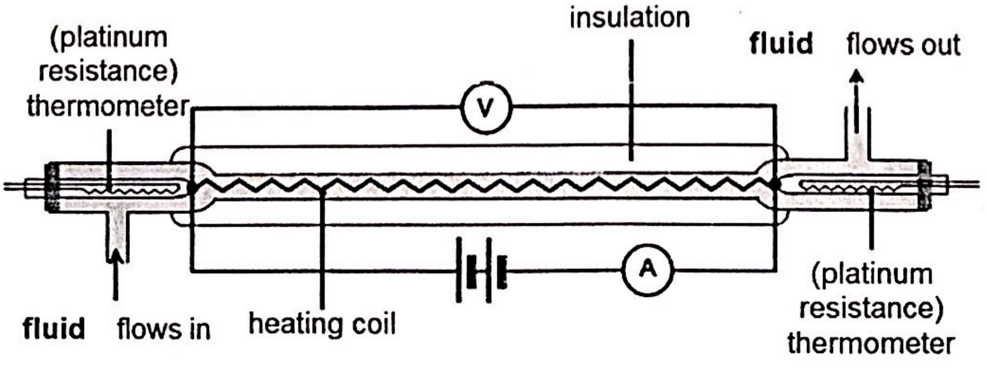
$$I\ V\ t = mc\left(T_f - T_i\right)$$

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

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 an electric heater, as in the following figure. 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 ~~of X~~ passing through in time *t*	m
inlet temperature	T_{in}
outlet temperature	T_{out}

Calculations

By the principle of conservation of energy,

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

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

Heat loss H depends on the excess temperature of the apparatus and the duration of the experiment.

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

Since heat loss to surroundings is proportional to the average excess temperature of the setup, the heat loss can be eliminated by repeating the experiment using the same inlet and outlet temperature and the same duration.

This means that in order to eliminate H, **the experiment has to be repeated with a different flow rate** and adjusting the power of the heating coil to such that the inlet and outlet temperatures remain at the same values as that of the first experiment.

	Previous Measurements	**New Measurements**
current	I	I'
potential difference	V	V'
time	t	
mass of X passing through in time t	m	m'
inlet temperature	T_{in}	
outlet temperature	T_{out}	

Further Calculations

new electrical energy supplied = **new** heat transferred + **HEAT LOSS**

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

Solving the simultaneous equations

$$I\,Vt - I'V't = (m - m')c\left(T_{\text{out}} - T_{\text{in}}\right)$$

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

Example 1 In an electrical constant flow experiment to determine the specific heat capacity of a liquid, heat is supplied to the liquid at a rate of 12 W. When the rate of flow is 0.060 kg min^{-1}, the temperature rise along the flow is 2.0 K.

(a) Calculate the specific heat capacity of the liquid.

(b) If the true value of the specific heat capacity is 5400 J kg^{-1} K^{-1}, estimate the percentage of heat loss in the apparatus.

a) by Principle of COE

electrical energy supplied = energy gained by liquid

$Pt = mc\Delta T$

$(12)(60) = (0.060)c(2.0)$

$c = 6000$ J kg^{-1} K^{-1}

b) If heat loss is to be considered,

in one minute,

$(12)(60) = (0.060)(5400)(2.0) + H$

$H = 72$ J

% heat loss = $\frac{72}{12(60)} \times 100\% = 10\%$

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.

a) by Principle of COE,

electrical energy transferred = heat transferred

in one minute, $IVt = mc(T_{out} - T_{in}) + H$

$(2.3)(3.3)(60) = \left(\frac{20}{[illegible]}\right)(22-18)(4200) + H$

$H = 119.4$ J

rate of heat loss = $\frac{119.4}{60} = 2.0$ J s^{-1} → same apparatus, → same heat loss

b) Since inlet & outlet temperatures are the same, the heat loss H is the same. ← same in/out T

by Principle of COE,

$IVt = mc_{oil}\Delta T + H$

in one minute

$(2.7)(3.9)(60) = (0.070)(c_{oil})(4) + 119.4$

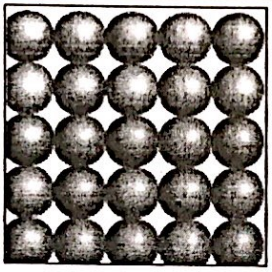
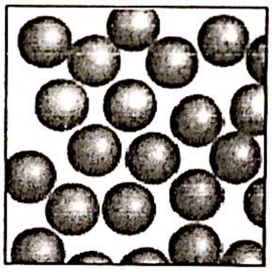
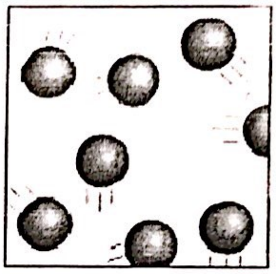
$c_{oil} = 1830$ J kg^{-1} K^{-1}

Kinetic Model of Matter

Matter is made up of many millions 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.

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

Characteristics of the three states of matter:

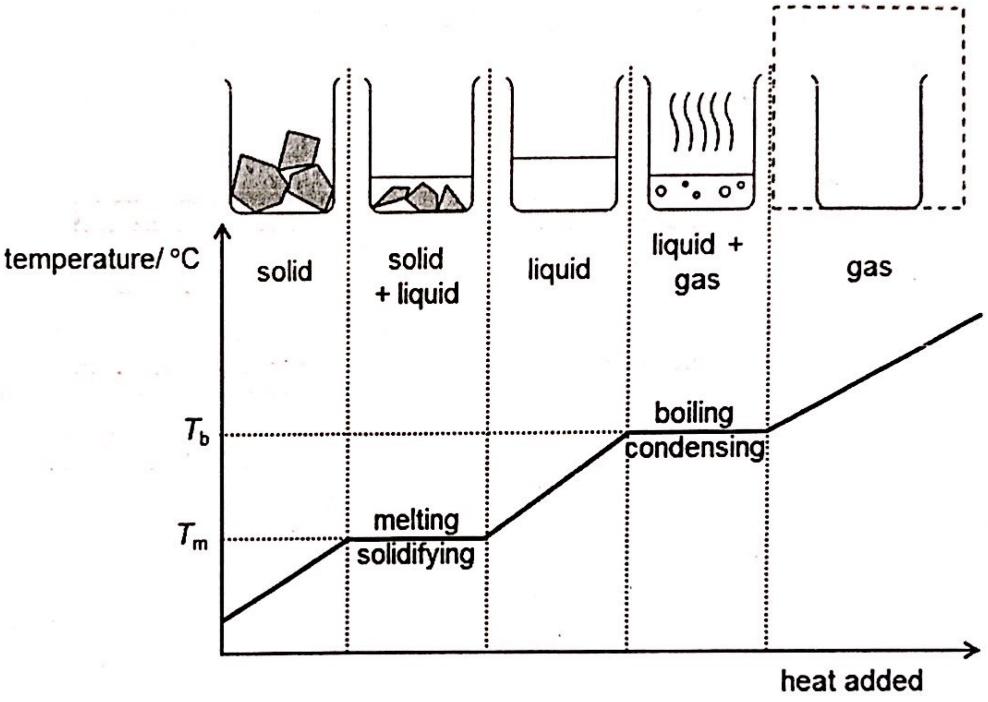
	Solid	**Liquid**	**Gas**
Packing Arrangement of Atoms/Molecules	Atoms/molecules are closely packed in a regular pattern called a lattice structure (regular, geometrical structure)	Atoms/molecules are slightly further apart than in solids	Atoms/molecules are very far apart
Illustration	 Crystal Lattice Structure	 Liquid atoms/ molecules	 Gas atoms/ molecules
Interatomic distance	$\approx 3\times10^{-10}$ m	$\approx 3\times10^{-10}$ m	Very far apart
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)
Kinetic Energy	**Vibrations of the atoms/molecules reflect their kinetic energy.**		
Effect of Temperature	**↑ Temperature = ↑ vibration = ↑ average kinetic energy**		

Change of Phase

The amount of heat required to bring about a change of phase is called latent heat.

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 or state at various points.



What happens during a change in phase:

	Melting	Boiling
transition	Solid to liquid	Liquid to gas
intermolecular interactions	Lattice structure has to break.	All bonds between atoms/molecules have to be <u>completely</u> broken.
at melting point or boiling point	• molecules have enough energy to vibrate so violently that the attractive forces cannot hold them together • the lattice structure collapses • change of state occurs	• thermal energy supplied is used to overcome the attractive forces between molecules • bonds are <u>completely</u> broken • change of state occurs
energy supplied	**Latent heat of fusion**	**Latent heat of vaporisation**
temperature	**At melting point and boiling point, the temperature remains constant.** This indicates that thermal energy supplied to the body is used to break bonds	

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 in the body of the liquid.

Application of Kinetic Model

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

- At *melting* point the molecules vibrate so violently that the attractive forces cannot hold them together, the lattice structure collapses and the solid undergoes a phase change.
- During this process, the energy supplied to the solid, called the *latent heat of fusion*, will not cause an increase in the temperature.
- This is because the energy is used to overcome the attractive forces between atoms and causes the lattice structure to break.
- The temperature remains constant during *boiling* as the heat supplied to the liquid is used to overcome the attractive forces between molecules and break the bonds completely.
- The energy required to change from the liquid state to the gaseous state is known as the *latent heat of vaporisation*.

2. 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 2.52×10^6 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 melting 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) to accomplish this. Energy is required by the gas to do work during the expansion process.

3. Why does a cooling effect accompany evaporation?

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

- The kinetic theory supposes that molecules of liquids are at continual motion and make frequent collisions with each other. During collisions, some molecules gain energy and others lose energy.
- If a molecule near the surface of the liquid gains enough energy, it will be able to escape from the attractive forces of the molecules ~~behind~~ below it.
- This results in a decrease in the average kinetic energy of the remaining molecules.
- Since temperature is a measure of the average kinetic energy of a material, the liquid will become cooler. That is, evaporation results in cooling.

Since the more energetic molecules escape, the average kinetic energy of the remaining molecules will be lower, which in turn results in a decrease in temperature.

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

Total kinetic energy = **10 J**

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

New total kinetic energy = **8 J**

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 kinetic energy of all the molecules);

(iii) causing a draught 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).

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 liquefy (or the liquid boil) without change of temperature. This is because the energy supplied is used to rearrange the molecules of the material. Once the change of state is completed, the temperature continues to rise if more energy is supplied.

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

Definition

The numerical value of 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 numerical value of 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

Latent heat of fusion: $l_f = \frac{Q}{m}$ S.I. unit is joule per kilogram (J kg^{-1})

Latent heat of vaporisation: $l_v = \frac{Q}{m}$ S.I. unit is joule per kilogram (J kg^{-1})

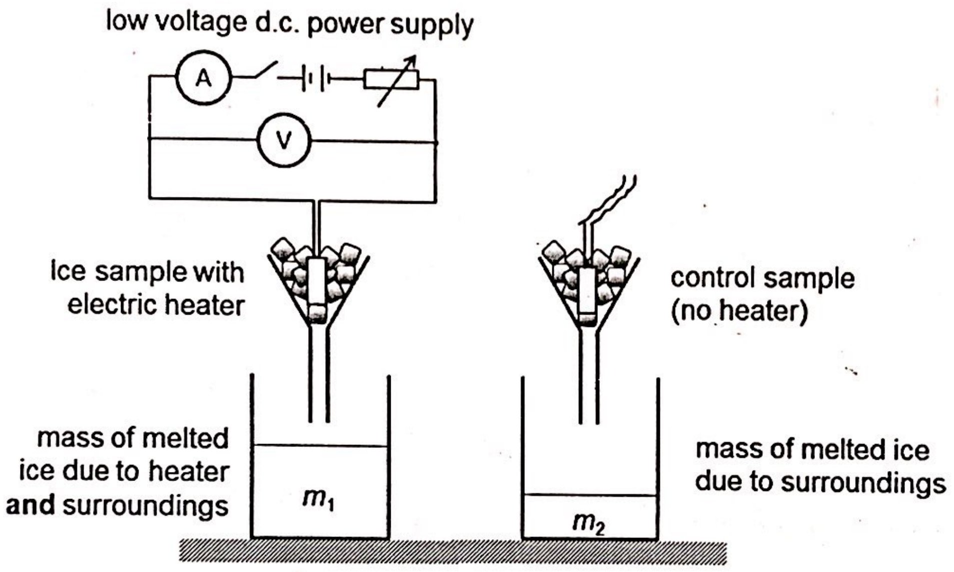
Determination of Specific Latent Heat by Electrical Methods

The main principles of determining specific latent heat by electrical methods involve heating a material through a change in phase and comparing it to the electrical energy supplied.

Latent heat of fusion

The solid in the funnel (in this case, ice) is heated electrically so that it melts at a steady rate. The melted liquid is collected in the beaker below. A rheostat (variable resistor) is used to ensure a steady heater current. Measurements are only taken once the rate of melting becomes steady.

Experimental Set-up



Measurements Taken:

current	I
potential difference	V
time	t
mass of melted ice due to heater and surroundings in time t	m_1
mass of melted ice due to surroundings in time t	m_2

Calculations

By the principle of conservation of energy

Electrical energy from heater + Heat from surroundings = Latent heat of fusion

$$IV \times t + m_2 l_f = m_1 l_f$$

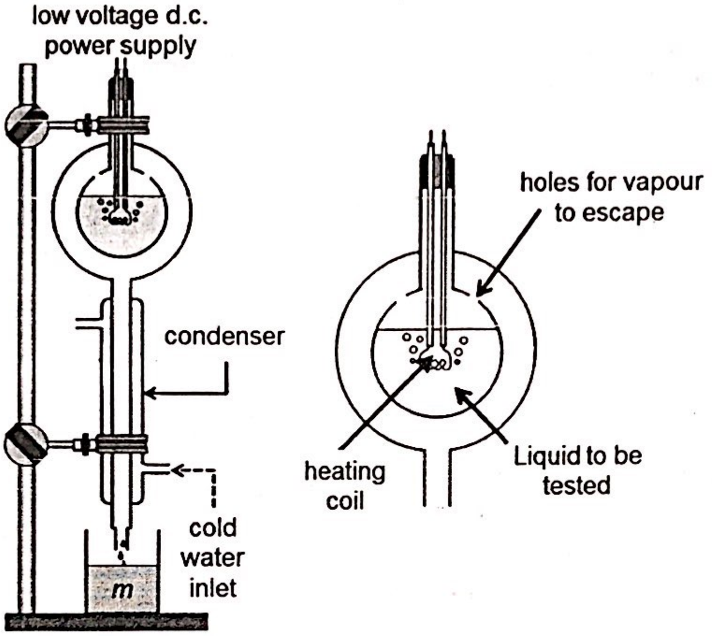
$$IVt = (m_1 - m_2) l_f$$

$$l_f = \frac{IVt}{m_1 - m_2}$$

Latent heat of vaporization

The liquid in the inner flask is heated electrically so that it boils at a steady rate. The vapour then passes through holes in the neck of the inner flask into the outer flask. Condensation takes place on the outer wall and in the condenser. The condensed vapour runs down the tube into a collecting flask.

Experimental Set-up



- A rheostat is used to ensure a steady heater current.
- Measurements are taken once the rate of vaporisation is steady.
- This can be determined once the rate of condensation of liquid in the collecting flask is steady.

Measurements Taken:

current	I
potential difference	V
time	t
mass of liquid collected in time t	m

Calculations

By the principle of conservation of energy

electrical energy supplied = amt of latent heat + HEAT LOSS

$$IV \times t = ml_v + H$$

Heat loss H depends on the excess temperature of the boiling liquid and the heating time. This means that in order to eliminate H, **the experiment has to be repeated with a different vaporisation rate** by adjusting the heating power. In the repeat experiment, the heat loss is the same since the boiling point of the liquid is the same and the heating time is also the same as before.

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

Further Calculations

New electrical energy supplied = **new** amt of latent heat + **same** HEAT LOSS

$$I'V' \times t = m' l_v + H$$

Solving for simultaneous equations

$$IVt - I'V't = (m - m')\, l_v$$

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

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 vaporization of water = 2.0×10^6 J kg^{-1})

by Prin of COE, energy from the heater is used to raise the temperature of water & kettle

a) $Q = mc\Delta T$

$(2000)(t) : (0.50)(4200)(100-20) + (400)(80)$

$t : 100s$

b) time the water is boiled for $: 300s - 100s : 200s$

energy released : $(200)(2000)$ ← by principle of CoE, $Pt : ml_v$

$: 4 \times 10^5$ J

mass of water boiled : $4 \times 10^5 \div 2 \div 10^6$

$: 0.20kg$

Example 4 A 600 W electric heater is used to raise the temperature of a certain mass of water from room temperature to 80 °C.

Alternatively, by passing steam from a boiler into the same initial mass of water at the same initial temperature, the same temperature rise is obtained in the same time. All the steam is produced at 100 °C and is totally condensed into water. 16 g of water were being evaporated every minute in the boiler.

Assuming that there were no heat losses, determine the specific latent heat of steam.

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

by applying the Prin of Con of E to both methods,

electric heater → $Pt = m_{water} c_{water} \Delta T_{water}$

steam → $m_{steam} l_v + m_{steam} c_{steam} \Delta T_{steam} = m_w c_w \Delta T_w$

$Pt : m_{steam} l_v + m_{steam} c_{water} \Delta T_{steam}$

$(600)(60) : (16)(10^{-3}) l_v + (16)(10^{-3})(4200)(100-80)$

$l_v : 2.17 \times 10^6 \ Jkg^{-1}$

Example 5 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 has been 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}.

$mc\Delta T$

energy loss of water = $(0.200)(4200)(40-70)$

$= -25200$ J

by P of COE,

energy gained by ice = 25200 J

$m l_f + mc\Delta T = (0.050) l_f + (0.050)(4200)(40)$

$= 25200$

$(0.050) l_f = 25200 - 6300$

$= 18900$

↳ need to take into account energy lost by flask, $c_{flask} \Delta t$

energy lost by water = $m_{water} c_{water} \Delta T$

energy lost by flask = $C_{flask} \Delta T$

energy required to melt ice = $m_{ice} l_v$

energy required to ↑T = $m_{ice} c_{water} \Delta T$

hence, by prin of CoE, heat loss by water = heat gained by the ice added the first time

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

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

$16800 + 30C_{flask} = 0.05 l_f$ — ①

heat loss by water = heat gained by ice added the 2nd time

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

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

$28140 + 30C_{flask} = 0.08 l_f$ — ②

② - ① :

$(0.08 - 0.05) l_f = 28140 - 16800$

$l_f = 378000$ J kg^{-1}

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

9.2 Internal Energy

Internal Energy

Definition

The internal energy of a system is determined by the state of the system. It can be expressed as the sum of the microscopic kinetic (translational, rotational and vibrational) and potential energies of the molecules of the system.

Microscopic Kinetic Energy

Molecules are in **constant motion** (translation, rotation and vibration) and hence have kinetic energy.

Temperature, which is a macroscopic concept, is actually a measure of the average kinetic energy of the molecules of a system. The faster the molecules move, the higher the temperature.

Microscopic Potential Energy

There may be attractive and repulsive forces (intermolecular interactions) between molecules. Hence, the molecules also have **potential energy** due to the **interactions** between them.

Since energy is required to break the interatomic or intermolecular bonds in order for phase changes from solids to liquids and liquids to gases, it can be deduced that solids have the most negative potential energy, followed by liquids and then gases.

Effect of Temperature

A rise in temperature implies an increase in the average kinetic energy of the molecules, which in turn implies an increase in the internal energy of the system.

NOTE

The kinetic and potential energies of the molecules in the system that make up the internal energy do not include those due to the bulk movement or position of the whole system.
E.g. For a cylinder of liquefied oxygen in a train, the internal energy of the oxygen 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.

Internal Energy of an Ideal Gas

In an ideal gas, the assumption is that there are no intermolecular interactions (no forces between the molecules). Hence an ideal gas has *negligible potential energy*.

The internal energy of an ideal gas is purely kinetic energy and is proportional to the amount of gas (N or n) and temperature T only.

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 $\boldsymbol{N}$ molecules: $\text{total } E_K = N \times \frac{1}{2}m\langle c^2 \rangle = \frac{1}{2}Nm\langle c^2 \rangle = \frac{1}{2}M_{\text{gas}}\langle c^2 \rangle$

$$\text{total } E_K = N \times \frac{3}{2}kT = \frac{3}{2}NkT$$

Since the internal energy U of an ideal gas is purely kinetic,

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

From the ideal gas equation,

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

As mentioned earlier, for a fixed amount of substance, U is determined by its state (p, V, T). Hence any changes in state (and/or amount of substance) will result in a change in internal energy ΔU.

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

- ΔU is solely dependent on thermodynamic temperature T
- Only a change in p or V which results in a change in T will result in a change in ΔU
- This is why the last permutation of the formula for the change in internal energy is $\Delta U = \frac{3}{2}\Delta(pV) = \frac{3}{2}\Delta[p_f V_f - p_i V_i]$

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

NOTE

- The factor of $\frac{3}{2}$ applies only to monatomic gases, i.e. gases 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 diatomic or polyatomic molecules,
  - The factor of $\frac{3}{2}$ does not apply
  - This is because the molecules now have microscopic potential energy (due to the bonds between the atoms) as well as rotational and vibrational motion, on top of the translational kinetic energy.

  (See Appendix for a brief discussion).

Example 6 Assuming that air behaves as an ideal gas,

(a) Show that the kinetic energy of a molecule of air at a temperature of 25 °C is 6.17×10^{-21} J.

(b) Hence, calculate the internal energy of one mole of the air at a temperature of 25 °C.

a) kinetic energy of one molecule of air

$= \frac{3}{2}kT$

$= \frac{3}{2}(1.38 \times 10^{-23})(25+273.15)$

$= 6.1717 \times 10^{-21}$

$= 6.17 \times 10^{-21}$ J (3s.f)

b) internal energy of one mole of air

= total translational kinetic energy of all the molecules

= KE of 1 molecule × no. of molecules

$= (6.1717 \times 10^{-21})(6.02 \times 10^{23})$

$= 3.7154 \times 10^{3}$

$= 3.72 \times 10^{3}$ J

9.3 First Law of Thermodynamics

Definition

The **First Law of Thermodynamics** states that 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.

word equation form.

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

mathematical equation form:

$$\Delta U = Q + W$$

Sign Conventions

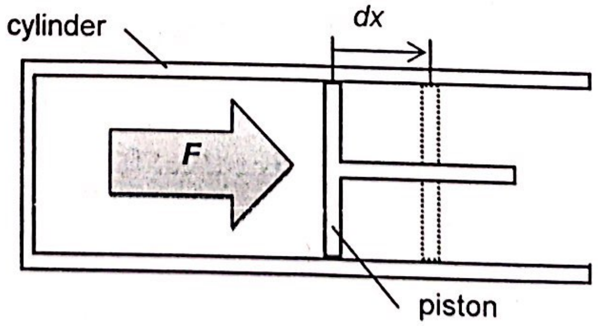
The First Law follows the convention as stated by its definition.

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.

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

Heat Q Heat is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings.

Work Done W Consider a system of gas in a cylinder with a frictionless, movable piston of 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 p.



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 <u>on</u> the gas

$$dW = -F\,dx = -(pA)\,dx = -p(A\,dx) = -p\,dV$$

For a finite change in volume from V_i to V_f, **work done <u>on</u> the gas** is simply the area under the pressure-volume (p-V) graph.

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

Example 7 The first law of thermodynamics may be expressed in terms of the equation $\Delta U = Q + W$.

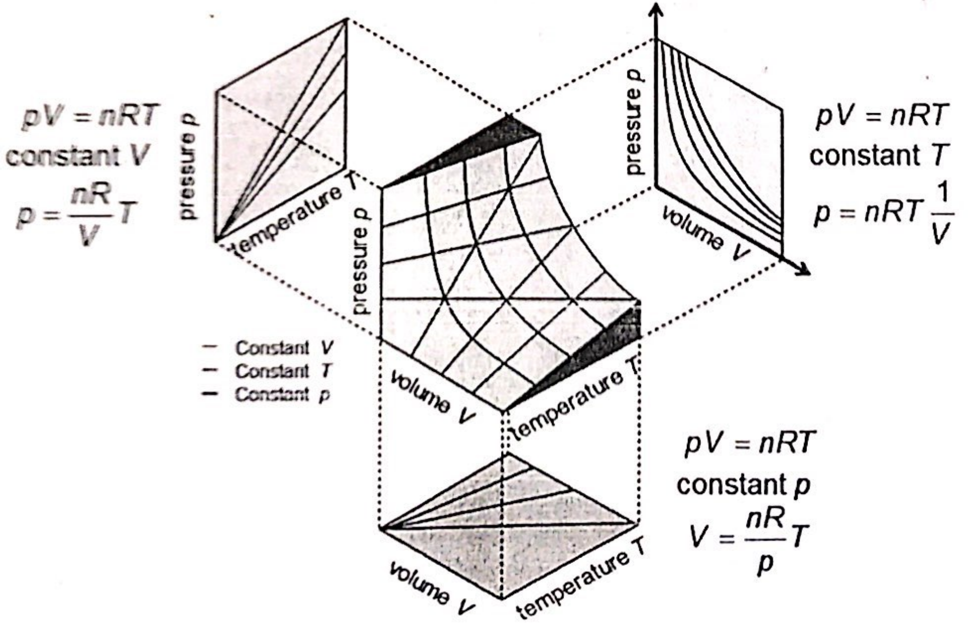
(a) Identify each of the terms in this equation.

(b) Some solids contract and some solids expand when they melt. Complete the table with the symbols + or – to indicate the signs of the thermodynamic quantities for each of the two types of solids when the solids melt at constant pressure.

Quantity	Solid which contracts on melting	Solid which expands on melting
ΔU	+	+
Q	+	+
W	+	–

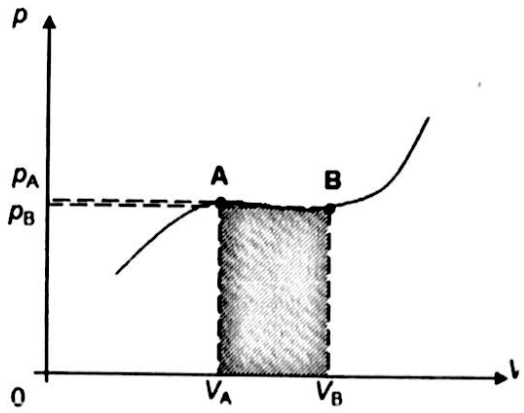
a) ΔU is the increase in the internal energy of the system
Q is the heat supplied to the system
W is the work done on the system

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



For the A-levels, we will concentrate only on graphical representations of the relationship between pressure and volume (i.e. the p-V graph).

Information from a *p-V* graph

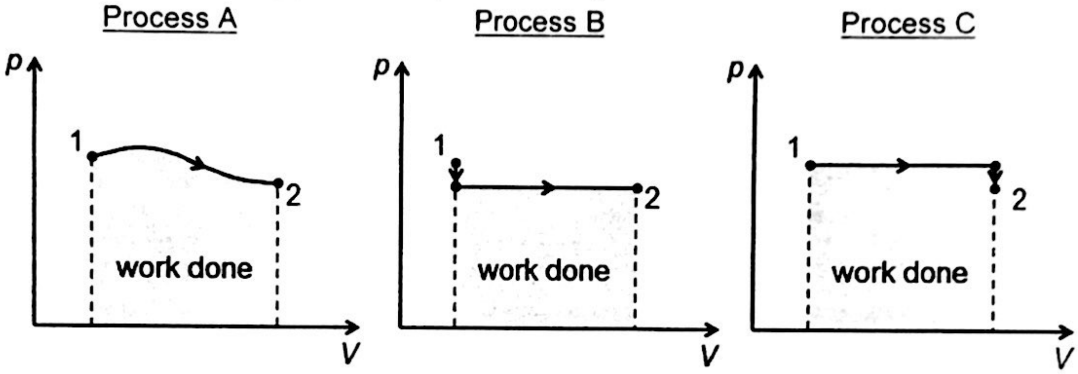


For a process from state **A** to **B**, the *p-V* graph gives us the following information:

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 moving from state 1 to state 2:



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

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

In summary,

- **Internal energy *U*** is dependent on state and independent of the path/process taken.
- **Work done *W***, on the other hand, is path dependent.

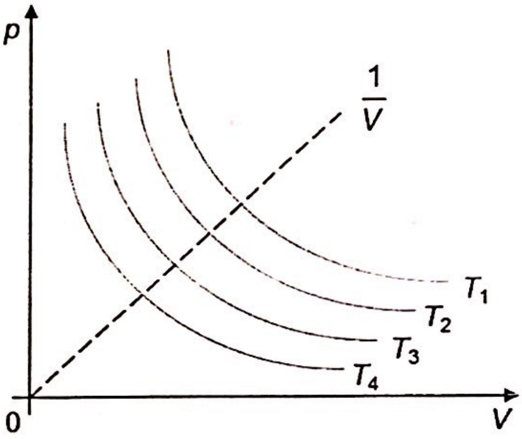
Special Processes

The following processes are special cases for a fixed amount of gas in a cylinder with a free moving piston.

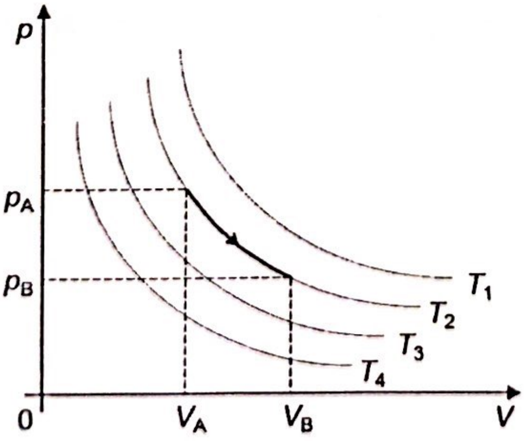
(1) Isothermal Process (*T* is constant)

If the change in the pressure and volume takes place without a change in temperature, the process is known as an *isothermal* change.

- Since temperature *T* is constant,
  $$\Delta U = 0$$
- Applying the ideal gas equation:
  $$pV = nRT \quad \Rightarrow p = (nRT)\frac{1}{V}$$
  At higher temperature *T*, (*nRT*) increases, plot of *p*-*V* shifts upwards
- Hence, $T_1 > T_2 > T_3 > T_4$
- Applying the first law of thermodynamics
  $$\Delta U = Q + W$$
  $$0 = Q + W$$
  $$\therefore Q = -W$$

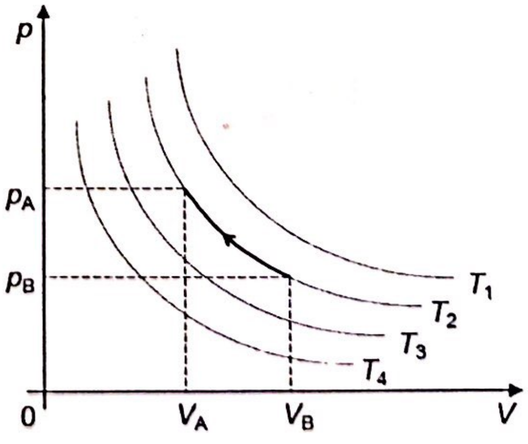


Isothermal Expansion



- *V* increases from V_A to V_B
  → Work is done by the system
  → *W* done **ON** the system is negative
- *Q* has to be transferred **TO** the system (positive) for this process to occur

Isothermal Compression



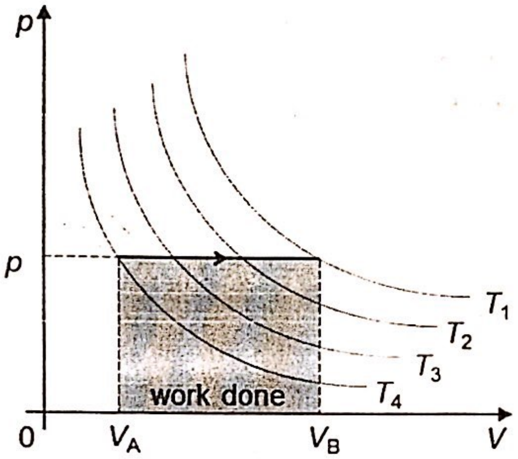
- *V* decreases from V_B to V_A
  → Work is done on the system
  → *W* done **ON** the system is positive
- *Q* has to be transferred **OUT** of the system (negative) for this process to occur

(2) Isobaric Process (p is constant)

If the volume change occurs at constant pressure, the area under the p-V graph is now a rectangle and the magnitude of the work done is thus $p\Delta V$.

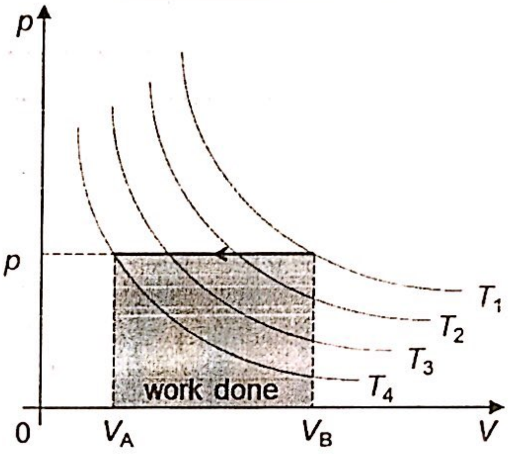
- Work done on a gas $W = -\int_{V_{\text{initial}}}^{V_{\text{final}}} p\,dV = -p\int_{V_{\text{initial}}}^{V_{\text{final}}} dV = -p\Delta V$

Isobaric Expansion



- V increases from V_A to V_B
  → $W = -p\Delta V = -p(V_B - V_A)$
- Work done **ON** the system is negative
- Temperature increases
  → Increase in internal energy ΔU is positive.
  → Heat Q is transferred to the system (positive).

Isobaric Compression



- V decreases from V_B to V_A
  → $W = -p\Delta V = -p(V_A - V_B)$
- Work done **ON** the system is positive
- Temperature decreases
  → Increase in internal energy ΔU is negative
  → Heat Q is transferred out of the system (negative).

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

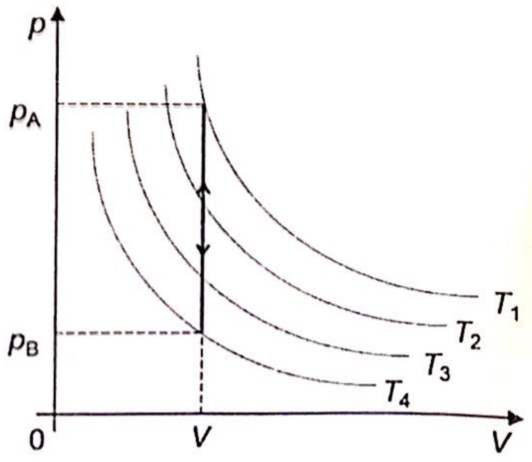
If the change in pressure occurs without a change in volume, the process is known as an *isovolumetric* or *isochoric* change.

- Since V is constant, $W = 0$.
- Applying the first law of thermodynamics

$$\Delta U = Q + W$$

$$\Delta U = Q + 0 \quad \Rightarrow \Delta U = Q$$

- If p decreases (from p_A to p_B)
  - Temperature will decrease
    → The increase in internal energy ΔU is negative
    → Heat Q is transferred out of the system (negative)
- If p increases (from p_B to p_A)
  - Temperature will increase
    → The increase in internal energy ΔU is positive
    → Heat Q is transferred to the system (positive)



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

When the change in pressure and volume occurs with no heat supplied to or lost from the system, the process is known as an *adiabatic* change. Such a change can be achieved 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

- No heat transfer means $Q = 0$.
- Note that $\Delta U \neq 0$
- Applying the first law of thermodynamics

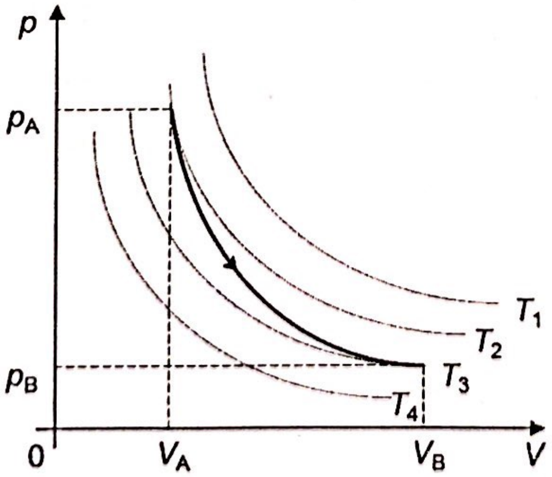
$$\Delta U = Q + W$$
$$\Delta U = 0 + W$$
$$\Delta U = W$$

  - A change in volume results in a change in temperature along with a change in pressure
  - Work is done at the expense of the internal energy of the system.
- Applying the ideal gas equation

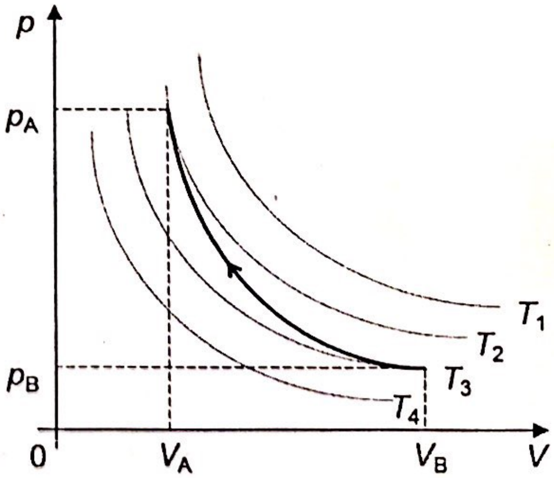
$$pV = nRT \quad \Rightarrow \frac{p_A V_A}{T_2} = \frac{p_B V_B}{T_3}$$

  - ALL values of *p*, *V*, *T* changes!

Adiabatic Expansion



Adiabatic Compression



- *V* increases from V_A to V_B

  → Work done **ON** the system is negative
- *p* decreases from p_A to p_B
- *T* decreases from T_2 to T_3

  → Increase in internal energy ΔU is negative

- *V* decreases from V_B to V_A

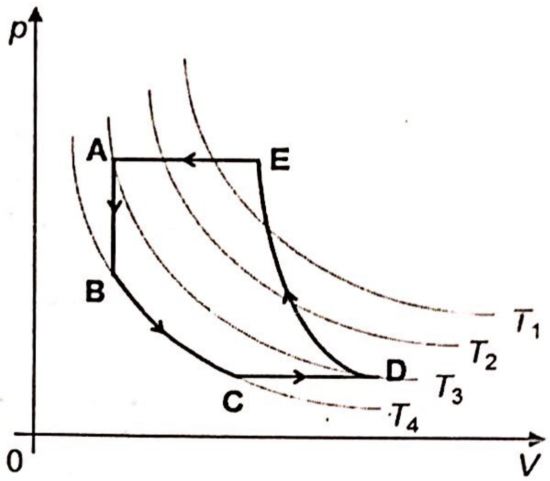
  → Work done **ON** the system is positive
- *p* increases from p_B to p_A
- *T* increases from T_3 to T_2

  → Increase in internal energy ΔU is positive

(5) Cyclic Process

A cyclic process is one by which the system goes through a series of processes and ends back at its beginning state.

A cyclic process is shown on the right, where the system goes through a cycle of processes and ends up at the same initial state (i.e. from $A \to B \to C \to D \to E \to A$).



- The system starts and ends at A
  → $\Delta U = 0$
- Total work done $W \neq 0$
  → $A \to B$: isovolumetric process, $\Delta V = 0 \therefore W_{AB} = 0$
  → $B \to C \to D$, expansion occurs $\therefore W_{BCD}$ (on the system) is negative
  → $D \to E \to A$, compression occurs $\therefore W_{DEA}$ (on the system) is positive
  → Since $|W_{BCD}| < |W_{DEA}|$, the net work done on the system (which is the area enclosed by the cycle!) is positive. i.e. $\therefore W$ is positive
- Applying the first law of thermodynamics

$$\Delta U = Q + W$$

$$0 = Q + W \quad \Rightarrow Q = -W$$

For this cycle of processes to occur, heat has to be transferred out of the system. There is net heat lost from the system.

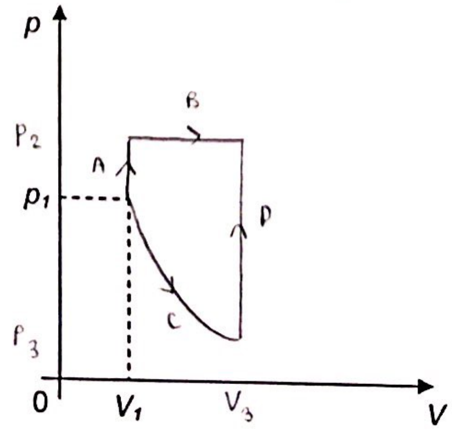
Example 8 A system of gas with pressure p_1, volume V_1, and temperature T_1 undergoes process A by being heated at constant volume to pressure p_2, volume V_1, and temperature T_2. It then undergoes an expansion by process B at constant pressure to pressure p_2, volume V_3, and temperature T_3.

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, characterised 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) both systems have the same internal energy at the end.
the internal energy of a system is dependent only on its state and nothing else.
since the 2 systems start from the same initial state and end up in the same final state, they have the same final internal energy

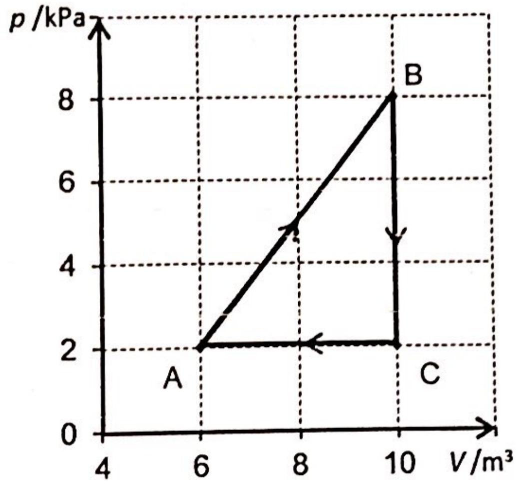
Example 9 A gas is taken through the cyclic process described in the graph below.

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

(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 a net WD by the gas.

WD by gas = area under the graph that is enclosed by the cycle

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

= 12 kJ

b) cyclic process (same initial & end state)

$\Delta U = 0$

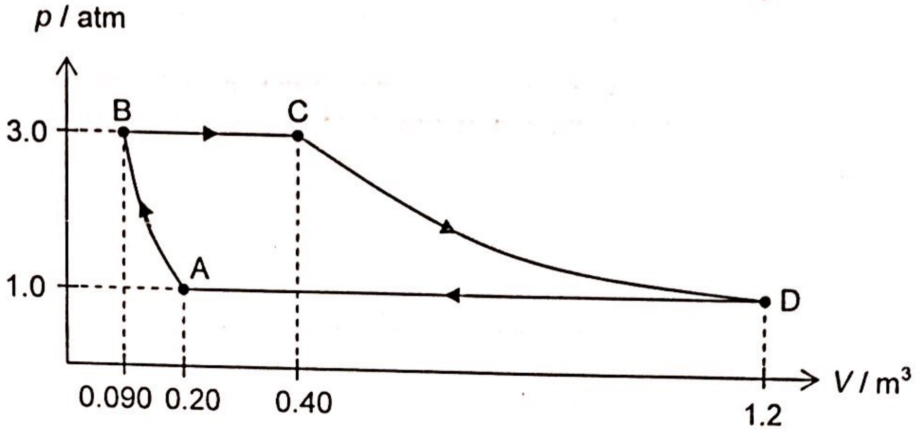
c) applying the first law of thermodynamics

$\Delta U = Q + W$

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

$Q = 12$ kJ

Example 10 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 100 kJ of energy entering the system. From C to D, the process is isothermal; from D to A, it is isobaric with 150 kJ of energy leaving the system.
(1 atm = 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	+106.4 kJ	+106.4 kJ
B → C	100.0 kJ	9.4 kJ	109.4 kJ
C → D	133.5 kJ	–133.5 kJ	0
D → A	–150.0 kJ	-101.3 kJ	251.3

5 ?.?

final - initial

$\Delta U = W_{AB} = -\left[\frac{3}{2}P_1V_1 - \frac{3}{2}P_2V_2\right]$

$= -\frac{3}{2}\left[1.013\times10^5 \cdot 0.2 - 0.09 \cdot 3 \cdot 1.013\times10^5\right]$

$= 106.4$

BC ~~$\Delta U = \frac{3}{2}(1.013\times10^5)$~~ $[$

$W = -p\Delta V$

$= (-3.0)(1.013\times10^5)(0.40-0.09)$

$= -9.42$ kJ

$\Delta U = \left(-\frac{3}{2}\right)(1.013\times10^5)\left[1.2 - 1.2\right] = 0$

$W = -p\Delta V = -(1.013\times10^5)(1.2-0.20)$

$= -1.013\times10^5$ J

$= -1.013\times10^2$ kJ

$= -101.3$ 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