Additional Notes

Section III Thermal Physics

Topic 9: First Law of Thermodynamics

Content:

- Specific heat capacity and 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 the 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.

Additional Notes

A Specific Heat Capacity

A.1 What is Specific Heat Capacity

- Heating is a process whereby thermal energy is being transferred.
- Thermal energy is transferred by conduction, convection or radiation from one body to another due to a temperature difference.
- When a body is heated, its temperature rise depends on:
  1. its mass - the smaller the mass, the larger the temperature rise for the same amount of heat supplied;
  2. the material of which the body is made - objects of the same mass but different materials experience different temperature rise when supplied with the same amount of heat. This is determined by a property called the specific heat capacity *c* of the body.

memorize

The **specific heat capacity *c*** of a substance is the thermal energy per unit mass per unit change in temperature of the substance.

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

$$Q = mc\Delta T$$

where Q = heat supplied
m = mass of the substance
ΔT = rise in temperature of the substance

- SI unit of c is J kg^{-1} K^{-1}.

The **heat capacity *C*** of a substance is the thermal energy required per unit change in temperature of the substance.

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

- SI unit of C is J K^{-1}.

Additional Notes

A.2 Practical Uses of Specific Heat Capacity

- For a given heat input, if it causes only a small temperature rise in the substance, this means the substance should have a high specific heat capacity.

- An example is the use of water as an efficient coolant in a car radiator. The specific heat capacity of water is 4.2×10^3 J kg^{-1} K^{-1} (i.e. 4.2×10^3 J of energy is required to increase the temperature of 1 kg of water by 1 K).

- The table below shows the mean specific heat capacity for some other materials at ordinary temperatures:

Mean Specific Heat Capacities / J kg^{-1} K^{-1}			
Aluminium	9.1×10^2	Ice	2.1×10^3
Copper	3.9×10^2	Rubber	1.7×10^3
Glass (ordinary)	6.7×10^2	Wood	1.7×10^3
Iron	4.7×10^2	Alcohol	2.5×10^3
Mercury	1.4×10^2	Glycerine	2.5×10^3
Lead	1.3×10^2	Paraffin oil	2.1×10^3

For relatively small changes in temperature, specific heat capacity *c* is approximately constant. However, over a wide range of temperature, the value of *c* for a substance may vary considerably. Unless stated otherwise, specific heat capacity is assumed to be constant.

Worked Example

An insulated electric kettle has a 2750 W element, and a heat capacity *C* of 530 J K^{-1}. 1.7 kg of water is placed in it. Determine how long it will take for the temperature of the water and kettle to rise from 20 °C to 100 °C. State any assumption(s) you have made in your calculations.
Specific heat capacity of water *c* = 4200 J K^{-1} kg^{-1}

In this topic, the working unit of temperature is the kelvin. When calculating the change in temperature there is no need to convert the unit to the kelvin scale since the change in degree Celsius is the numerically the same as a change in Kelvin

Solution

Energy supplied = Energy gained by water + Energy gained by kettle

$$Pt = mc\Delta T + C\Delta T$$

$$2750\,t = (1.7)\,(4200)\,(100\text{-}20) + (530)\,(100\text{-}20)$$

$$t = 223 \text{ s}$$

Assumption: Negligible thermal energy is lost to the surroundings

Additional Notes

Example 1

A copper cube of mass 110 g is heated to a temperature of 100 °C and then rapidly transferred to an insulated aluminum can of mass 80 g containing 200 g of water at 10 °C. Calculate the final steady temperature of the cube and water, assuming that heat loss to the surroundings is negligible. (14 °C)

Substance	Specific heat capacity
Water	4.2×10^3 J kg^{-1} K^{-1}
Aluminum	9.1×10^2 J kg^{-1} K^{-1}
Copper	390 J kg^{-1} K^{-1}

Thinking Process

What are the energy transfer processes occurring in this system?

- The copper will lose energy, while the water and the aluminium can will gain energy.
- The final steady temperature is hence lower than 100 °C but higher than 10 °C.

What is the implication for the negligible heat loss to the surroundings?

- The total energy of the system is conserved.
- Hence, the heat loss by the copper is equal to the heat gain by the water and aluminium.

Hint: *always start by writing a word equation containing all the gains and losses of energy*

Additional Notes

B Specific Latent Heat

- In some situations, supplying (removing) thermal energy to (from) a body does not result in an increase (decrease) in temperature but **a phase change** takes place.

- In the process, the supplied (removed) thermal energy is absorbed (released) as **latent heat of vaporization or fusion** at a constant temperature.

Latent heat, l, of a substance is the thermal energy transferred to change the substance from one phase to another, without any change in temperature.

The **specific latent heat of fusion, l_f**, of a substance is the thermal energy per unit mass required to change it from solid to liquid without change of temperature

memorize

The **specific latent heat of vaporisation, l_v**, of a substance is the thermal energy per unit mass required to change it from liquid to gas without change of temperature.

memorize

- Thus, if an amount of heat Q is needed to cause a change in state of mass m of a substance, then the specific latent heat l of the substance is given by:

$$l = \frac{Q}{m}$$

$$Q = m\,l$$

The latent heat of vaporization and fusion also refers to the amount of energy **released** by a substance when it changes from a gas to a liquid, & from a liquid to a solid respectively.

- SI unit of l is J kg^{-1}.

Example 2

Calculate the heat needed to completely vaporise 200 g of water at a temperature of 30 °C to form steam at a temperature of 100 °C.
Specific heat capacity of water = 4200 J kg^{-1} K^{-1}
Specific latent heat of water = 2260 kJ kg^{-1}

Thinking Process
What are the processes involved here?
Energy is absorbed by the water to raise its temperature from 30 °C to 100 °C first.
Thereafter, energy is absorbed to vaporise the liquid water into its gaseous state.

Additional Notes

Bulk KE or Bulk PE refers to KE or PE due to the entire object and not due to random motion of particles. E.g. KE of an object falling to Earth is not due to random motion of particles and hence not part of internal energy.

C Internal Energy

C.1 What is Internal Energy

- Internal energy *U* of a system is associated with the energy of its constituent particles on the microscopic scale, does not include bulk kinetic energy or bulk gravitational potential energy

> Internal energy is the sum of:
> 1. the kinetic energy E_k due to the random motion of the atoms / molecules and
> 2. the potential energy E_p due to intermolecular / inter-atomic forces between them.

- That is,

$$U = E_k + E_p$$

- By Principle of Conservation of Energy, once heat is supplied to a body, it will be converted and stored as internal energy of the body.

- An **increase in internal energy** results in either a rise in temperature or a change of state of the body.
  - Recall Topic 11.1.1, the temperature of a system is a measure of its average molecular kinetic energy. A higher temperature implies that the molecules in the system are moving faster on the average. Thus there is an **increase in the average kinetic energy of the molecules**.

  - **Changing state** (melting, freezing, boiling, condensation, sublimating, etc) involves **changes in the potential energy in molecules**.

Check your understanding 1

A helicopter is flying at a constant altitude and speed. The air in the helicopter has
50 MJ of potential energy due to the altitude of the helicopter,
-2 MJ of potential energy due to the intermolecular attraction between the air molecules,
5 MJ of kinetic energy due to the motion of the helicopter,
20 MJ of kinetic energy due to the random movement of the air molecules.

What is the internal energy of the air in the helicopter?
A 18 MJ **B** 22 M J **C** 73 MJ **D** 75 MJ **E** 77 MJ

Additional Notes

Additional Notes

C.2 Internal Energy ΔU of An Ideal Gas

- For an ideal gas, the intermolecular forces are negligible except during collisions. This implies that the potential energies arising from the distribution of the particles in the system is also negligible. $E_p = 0$.
- Hence, the internal energy of an ideal gas is made up only by the sum of the random KE possessed by the particles in the system

  $U = E_k + E_p = E$ where E_p is zero for an ideal gas.

- Recall from the topic of Temperature and Ideal Gases, for an ideal gas,
  mean KE of gas molecule $\propto$ T

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

- For an ideal gas of N molecules (or n moles), internal energy = total KE of molecules

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

  where $Nk = N\frac{R}{N_A} = nR$

- since Boltzmann constant $k = \frac{R}{N_A}$ and $n = \frac{N}{N_A}$ where N_A is Avogadro constant
- The increase in internal energy can thus be written as

  $$\Delta U = U_f - U_i = \frac{3}{2}nRT_f - \frac{3}{2}nRT_i = \frac{3}{2}nR\Delta T$$

  $$\boxed{\Delta U = \frac{3}{2}nR\Delta T}$$

- This equation applies only for ideal gases. It is not applicable for other systems that are not ideal gas. For example, an object that undergoes a phase change, temperature remains constant, but since the intermolecular potential energies of its molecules will change, its internal energy will change.

Check your understanding 2

A certain mass of ideal gas has internal energy U. The gas is compressed to half its original volume while keeping its temperature constant. What is the internal energy of the ideal gas after compression?

A ¼ U **B** ½ U **C** U **D** 2 U E 4U

Additional Notes

D First Law of Thermodynamics

- In this section, we are concerned with how the internal energy of a system can be changed.

First Law of Thermodynamics is applicable to all systems and not restricted to ideal gas only, unlike ideal gas equation/equation of state.

- In general, the internal energy of a system depends on its **state (pressure, volume & temperature)** i.e. ***p***, ***V*** & ***T*** and there are two processes which can result in an increase in internal energy:

  1. heat absorbed by the system
  2. work done on the system

- Conversely, there are two processes which can result in a decrease in internal energy:

  1. heat released by the system
  2. work done by the system

- The First Law of Thermodynamics states that the increase in internal energy ΔU of a system is the sum of the heat absorbed by the system Q and the work done on the system W.

There are different ways of stating First Law of Thermodynamics, depending on the direction of energy transfer. Important point is to ensure that, when stating the law, the correct directions of energy transfer for all 3 quantities are make clear.

$$\Delta U = Q + W$$

where ΔU = **increase** in internal energy
Q = heat **absorbed by** the system or heat **supplied to** system
W = work done **on** the system

- The First Law of Thermodynamics is a statement of the Principle of Conservation of Energy. Whenever a certain amount of heat is supplied to a system and/or a certain amount of work is done on the system, it will result in an equivalent amount of increase in its internal energy because energy must be conserved.

- It is important when applying the law to get the signs correct.

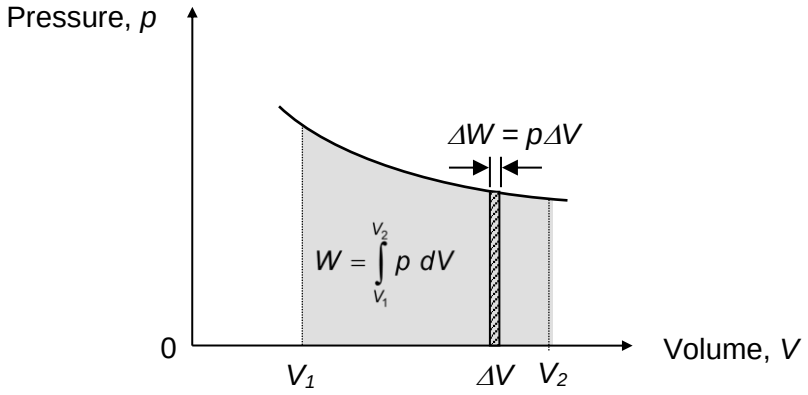
	ΔU **Increase in internal energy**	***Q*** **Heat**	***W*** **Work done**
Positive (+)	System gains internal energy	System absorbs heat	Work is done ON system
Negative (-)	System loses internal energy	System gives off heat	Work is done BY system

Additional Notes

D.2 Work done by a Gas

- The work done by the gas expanding a volume ΔV against a constant pressure p is
  $W = p\,\Delta V$
  i.e. the product of pressure and change in volume of the gas.

- For varying pressure p,



In general, the total work done by gas when the volume increases from V_1 to V_2 is given by

$$W = \int dW = \int_{V_1}^{V_2} p\,dV$$

- The area under a p-V graph represents the work done.

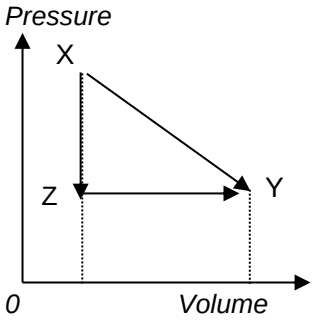
- To find work done using a graph, make sure that the graph is a ***p* vs *V*** graph. Take care of the **units used**. The units of work done is Joules (J) only if units of pressure is given in Pa and volume is in m^3. Check the axes and units carefully!

- Note the following sign conventions for work done in expanding / compressing a gas:

	When the gas expands	**When the gas is compressed**
Change in Volume ($V_{final} - V_{initial}$)	> 0 (positive)	< 0 (negative)
Work done by the gas is…	positive	negative
Work done on the gas is…	negative	positive
Work is done…	by the gas	on the gas

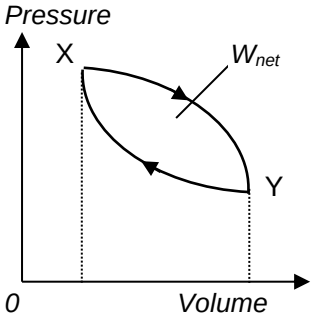
Additional Notes

- Work done on/by the gas and the energy supplied/taken depend on the path taken for the change. However, the **change in internal energy is path independent** because it **depends solely on the state** the system is in. Hence, only the **initial and final state** variables (*p*, *V*, *T* and *n*) at equilibrium are considered. In the graph below, if the change is from X to Y compared to X to Z to Y, the change in internal energy will be identical.



Quick tip: Cyclic processes represents a closed loop graphically. For p-V graph (note: it is not applicable for V-p graph): A clockwise loop represents net work done by gas since more work done by gas than on gas. An anticlockwise loop represents net work done on gas since work done on gas is more than work done by gas.

- If a system of gas is taken through a round trip, i.e., a cyclic process, the **area enclosed gives the net work done**.



Check your understanding 3

Fig. 1, 2 and 3 show the *p*-*V* curve for a gas.
For each *p*-*V* curve, determine if the work done on the gas is positive, negative or zero.

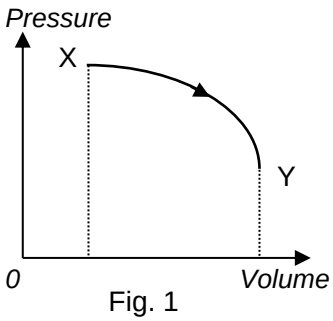


Fig. 1

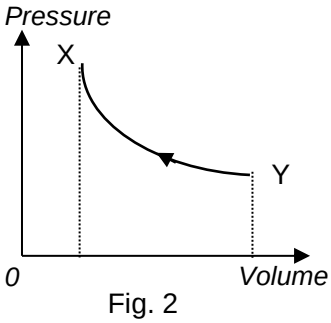


Fig. 2

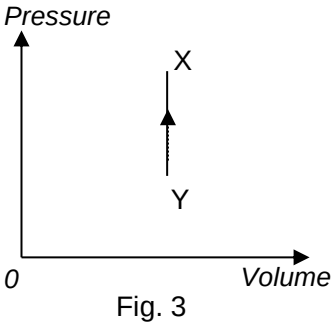


Fig. 3

Additional Notes

Worked Example

A sample of gas is enclosed in a cylinder by a frictionless piston of area 60 cm^2. The cylinder is heated so that 400 J of heat is supplied to the gas. The gas then expands against atmospheric pressure and pushes the piston 20 cm along the cylinder.

Given that atmospheric pressure is 1.0×10^5 Pa, calculate

(a) the work done by the gas and (120 J)

(b) the change in internal energy of the gas. (280 J)

Solution

(a) Work done by gas at constant pressure

$= p \Delta V$

$= p \times A \times \Delta L$

$= 1.0 \times 10^5 \times 60 \times 10^{-4} \times 20 \times 10^{-2}$

$= 120$ J

(b) System ABSORBS heat (positive Q); work is done BY system (negative W)

$\Delta U = Q + W = (+400) + (-120) = 280$ J

Hence, the internal energy of the gas increases by 280 J.

How is work done by a gas calculated?
The most general method to determine work done by a gas is the area under its pressure-volume graph.
For a gas maintained at constant pressure, the work done is also given by $p\Delta V$.
Take note of the sign convention for the work done by gas – for expansion, work done by gas has a positive value.

Why does the internal energy of the gas increase by less than 400 J?
Although heat is supplied to the gas, energy is expended by the gas because it needs to do work against the atmosphere when it expands.
Overall, part of the energy supplied through heating is expended through work done. Hence, the internal energy increases by less than 400 J.

Example 3

At a temperature of 100 °C and a pressure of 1.01×10^5 Pa, 1.00 kg of steam occupies 1.67 m^3 while the same mass of water occupies 1.04×10^{-3} m^3. The specific heat of vaporization of water at 100 °C is 2.26×10^6 J kg^{-1}. For a system consisting of 1.00 kg of water changing to steam at 100 °C and 1.01×10^5 Pa, determine

(a) the heat supplied to the system, (2.26×10^6 J)

(b) the work done by the system, (1.60×10^5 J)

(c) the increase in internal energy of the system. (2.09×10^6 J)

What are the processes occurring in the system?
Latent heat is absorbed by the water in order to effect the state change.
As the water turns into steam, there is significant expansion and hence, work is done by the steam against the atmosphere.

Latent heat of vaporisation represents the amount of thermal energy required to cause phase change. However, not all of this energy will be stored as internal energy since some may be used to do work against environment. Hence, latent heat may not be equal to change in internal energy.

Additional Notes

E Thermodynamic Processes

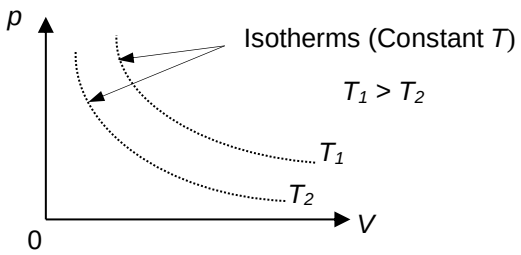
- A thermodynamic process is a process whereby a system changes from an initial equilibrium state to another final equilibrium state.

- The following special cases are considered for a system of fixed mass of ideal gas in a cylinder with a free moving piston. A thermodynamic process is said to have taken place when a system changes from an initial equilibrium state (pressure, volume & temperature) to another final equilibrium state.

  According to the Equation of State or Ideal Gas Law,

$$pV = nRT$$

$$p = \frac{nRT}{V}$$



- Some thermodynamic processes that a gas can undergo include:

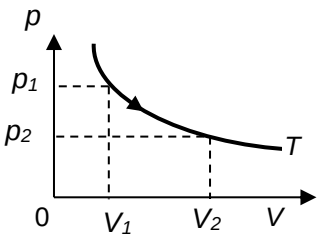
  1. **<u>Isothermal Process</u>** – temperature remains constant by submerging system in an external constant temperature environment, or if change takes place slowly, allowing temperature to equalize with surrounding

     - A constant temperature implies that there is <u>no change in the average molecular kinetic energy</u> of the system.

     - For an <u>ideal gas</u>, the internal energy is composed of molecular kinetic energy only (no potential energy component). As such, constant temperature implies <u>no change in internal energy, i.e.</u>

$$\boxed{\Delta U = 0}$$

     - In this case, the First Law of Thermodynamics simplifies to

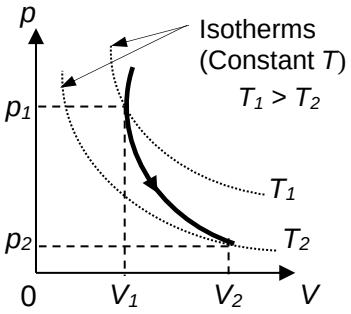


$$\Delta U = Q + W = 0 \quad \Rightarrow \quad Q = -W$$

     - This means that the heat (Q) absorbed by an ideal gas during an isothermal expansion is equivalent to the mechanical work done ($-W$) by the gas

     - Alternatively, work is done by the ideal gas at the same rate as heat is supplied to it such that there is no net change in its internal energy.

2. **<u>Adiabatic Process</u>** – change occurs so quickly that no heat flows into or out of the system or the piston is insulated



- Since there is no net heat flow into or out of the system,

$$Q = 0$$

- The First Law simplifies to $\Delta U = 0 + W$

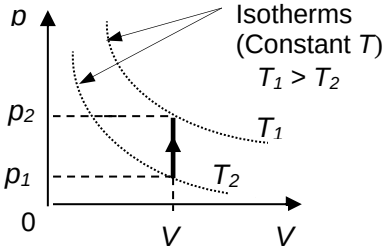
$$\Rightarrow \quad \Delta U = W$$

- The above equation implies that <u>the change in internal energy of the system during an adiabatic process is entirely due to the work done on it</u>.

- In an <u>adiabatic expansion</u>, work is done by the gas wholly at the expense of its internal energy. As such, the internal energy decreases and the gas cools.

- In an <u>adiabatic compression</u>, all the work done on the gas by the compressing agent appears as an increase in internal energy of the gas. Therefore, there is a rise in its temperature.

3. **<u>Isochoric Process</u>** – piston is stationary and volume remains constant as temperature changes.



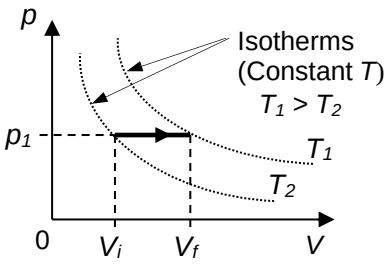
- Since there is no change in volume, no work is done

$$W = 0$$

- Therefore, $\Delta U = Q$

- All the heat absorbed by the system results in an increase in its internal energy by the same amount.

4. **<u>Isobaric Process</u>** – pressure remains constant by having a movable piston to vary volume as temperature changes.



- Work done on the gas: $W = -\boldsymbol{p}(\boldsymbol{V}_f - \boldsymbol{V}_i)$

- Some of the heat supplied to the gas increases the internal energy and the rest is used to do work.

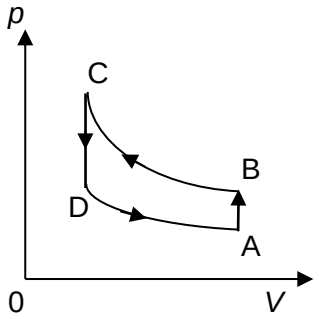
Additional Notes

F Cyclic Processes

- These are the processes in which, after certain interchanges of heat and work, the system is restored back to its initial state. Cyclical processes form a closed loop on a pressure-volume graph.

- Final temperature = initial temperature $\Rightarrow$ $\Delta \boldsymbol{U} = 0$ (internal energy is unchanged)

- From 1st law of thermodynamics $\Rightarrow$ $\boldsymbol{Q} = -\boldsymbol{W}$

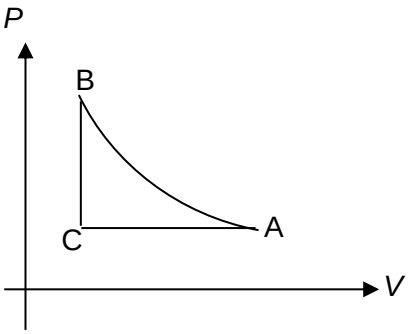


- The table below summarizes the characteristics of the processes:

Process	Condition	Implication
Constant volume	$\boldsymbol{W = 0}$	$\boldsymbol{\Delta U = Q}$
Constant pressure	$\boldsymbol{W = -p(\Delta V)}$	$\boldsymbol{\Delta U = Q + W}$
Isothermal	$\boldsymbol{\Delta U = 0}$	$\boldsymbol{Q = -W}$
Adiabatic	$\boldsymbol{Q = 0}$	$\boldsymbol{\Delta U = W}$
Closed cycle	$\boldsymbol{\Delta U = 0}$ Or that: Sum of all $\Delta U = 0$	$\boldsymbol{Q = -W}$ *Eg:* $\boldsymbol{\Delta U_{A\to B} + \Delta U_{B\to C} + \Delta U_{C\to D} + \Delta U_{D\to A} = 0}$

Check your understanding 4

An ideal gas undergoes some thermodynamic processs as shown in the P-V diagram below.



(i) If the gas undergoes a cycle of changes A → B → C → A, Which of the following statement about the increase in internal energy of the gas $\Delta \boldsymbol{U}$ is correct?

A ΔU is positive
B ΔU is negative
C ΔU is zero
D ΔU cannot be determined

Additional Notes

After arriving at the solution for (ii), think about the differences in W and in Q for path ABC vs path AC.

(ii) The gas can change its state from A to C either through path 1 (A → B → C) or path 2 (A → C).

Which of the following statement about the increase in internal energy of the gas ΔU is correct?

A ΔU for Path 1 is less than ΔU for Path 2

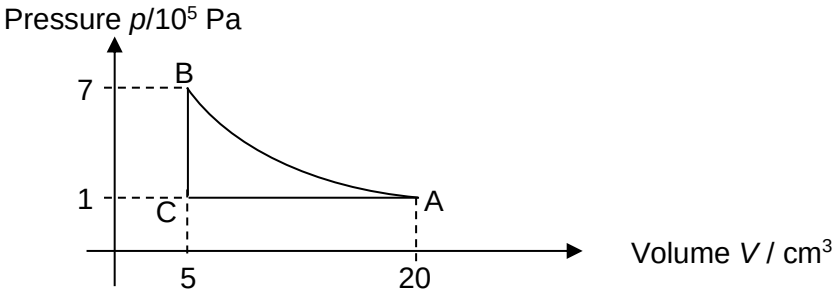
B ΔU for Path 1 is more than ΔU for Path 2

C ΔU for Path 1 and ΔU for path 2 are both zero

D ΔU for Path 1 and ΔU for path 2 are the same.

Example 4

An ideal gas undergoes a cycle of changes A → B → C → A, as shown in the figure below.



The table below shows the energy changes during one cycle. Complete the table.

Section of cycle	Heating supplied to gas / J	Work done on gas / J	Increase in internal energy of gas / J
A → B	Zero	4.2	
B → C	−8.5		
C → A			
Net			

Thinking Process

How is work done calculated from a *p-V* graph?
The area under the graph gives the work done. As the process C to A is an expansion, the work done by the gas is positive, hence work done on gas is negative.

Apply the First Law of Thermo-dynamics to complete the table.

Additional Notes

Relating Science and Society

Every time you commute in a gasoline-powered car, turn on an air conditioner, or cook a meal, you reap the benefits of thermodynamics, the study of relationships involving heat, mechanical work, and other aspects of energy and energy transfer. As much as we have applied this field of study to make our lives more comfortable, an inevitable consequence of these energy conversions is the discharge of heat, leading to thermal pollution in our environment. One approach to reduce this is the development of alternative sources of energy, e.g. solar power. Another approach is to make things more efficient. Reducing the demand for energy should also be a personal and policy priority. We can all play our part by embracing the three Rs – Reduce, Reuse, Recycle.

Some Useful Equations and further reading

Thermal Properties	Heat $Q = mc\Delta T$ or ml_f or ml_v
1st Law of Thermodynamics	$\Delta U = Q + W$
Work done by gas	$W_{by\ gas} = p\Delta V$ (for constant p only) or area under p-V graph (for all cases)
Ideal Gas Equation or Equation of State	$pV = nRT$ $pV = NkT$
ΔU for an monatomic ideal gas	$\Delta U = \frac{3}{2}nR\Delta T$

The following are **optional** content for further reading. They are closely related to this topic, but not explicitly covered by the syllabus.

1. Using the kinetic model (a microscopic model) to explain the following macroscopic phenomena:
    i. Why do melting and boiling take place without a change in temperature?
    ii. Why is the specific latent heat of vaporisation higher than specific latent heat of fusion for the same substance?
    iii. Why does cooling effect accompany evaporation?

2. Determination of Specific Heat Capacity and Specific Latent Heat by Electrical Methods
3. Derivation of the equation $W = p\Delta V$ for work done by a gas expanding against a constant pressure.

You can access the content via the QR code: