

11. Thermal Properties of Materials

Content

- 11.1 Specific heat capacity
- 11.2 Specific latent heat capacity

- 11.3 Internal energy

- 11.4 First law of thermodynamics

Learning Outcomes

Candidates should be able to :

- (a) explain using a simple kinetic model for matter why melting and boiling take place without a change in temperature,
 - (i) the specific latent heat of vaporisation is higher than the specific latent heat of fusion for the same substance,
 - (ii) cooling effect accompanies evaporation.
- (b) define and use the concept of specific heat capacity, and identify the main principles of its determination by electrical methods.
- (c) define and use of the concept of specific latent heat, and identify the main principles of its determination by electrical methods.
- (d) relate a rise in temperature of a body to an increase in its internal energy.
- (e) 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.
- (f) recall and use the first law of thermodynamics expressed in terms of change in internal energy, the heating of the system and the work done on the system.

- The kinetic model for matter assumes that matter is made up of particles (atoms or molecules) in continual motion.

- The atoms or molecules in a material have two kinds of energies: (i) kinetic energy E_k and (ii) potential energy E_p .

- the kinetic energy is due to their continual motion which may be translational, vibrational (about their equilibrium positions) or rotational.

- The kinetic energy of the molecules is determined by the temperature of the material.
Higher temperature \Rightarrow higher kinetic energy E_k .

- the potential energy is due to the intermolecular forces which hold the molecules together.

- The potential energy is stored in the interatomic bonds that are continuously stretched and compressed as the atoms vibrates and it depends on the interatomic forces between the atoms and their separation.

- E_k and E_p are collectively referred to as the internal energy.

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- The internal energy of a body is the sum of the random distribution of all the potential and kinetic energies of the atoms and molecules in the body.

$$U = E_k + E_p$$

- when E_k changes \Rightarrow temperature changes,
when E_p changes \Rightarrow there is a change of state.

- When heat is transferred to a body, the internal energy of the body increases. The increase in internal energy may be used (i) to increase the random motion of the atoms or molecules, resulting in an increase of the temperature and/or (ii) to separate the atoms or molecules further apart hence increasing their potential energy.

- In solids and liquids both forms of energies are present and there is a continuous interchange between the E_k and E_p .

In a gas, where the intermolecular forces are much weaker, the internal energy is almost entirely E_k .

In an ideal gas, the internal energy is entirely kinetic as there is no intermolecular forces.

Change of State & Latent Heat

- Matter generally exists in three states: solid, liquid and gaseous.
- The state of matter depends on its temperature and the pressure exerted on it.
- A transition from one state to another is known as a change of state or a phase change.
- The heat which a body absorbs in melting, boiling and gives out in freezing or condensing is called latent (hidden) heat because it does not produce a change in the temperature of the body.
- Latent heat is defined as the heat energy absorbed or liberated by a substance in order to change a substance from one phase to another phase without a temperature change.
- During phase change, melting and boiling, latent heat is involved:
 - to weaken and/or break the intermolecular bonds,
 - to cause the system to expand against the atmosphere.

Melting - change of phase from solid to liquid

- (i) As heat is supplied to a solid, the molecules vibrate more and more vigorously and the temperature of the solid rises. As the supply of heat continues, the molecules will eventually overcome the forces between them. Hence the regular crystalline structure of the solid breaks down and the solid melts.
- (ii) At melting point, there is no increase in temperature even though heat, called latent heat of fusion, is being absorbed.
- (iii) The heat energy is used as work to overcome the forces of attraction between the molecules; the molecules then can move more freely and exhibit greater disorder that characterise the liquid state.
- (iv) the supply of latent heat is regarded as increasing the potential energy component since it allows the molecules to move further apart.

The specific latent heat of fusion L_f of a substance is defined as the quantity of heat required to change unit mass of the substance from the solid state to the liquid state without a change in temperature.

S I unit of L_f : J kg^{-1}

$$\begin{aligned}L_f \text{ of ice} &: 3.34 \times 10^5 \text{ J kg}^{-1} \\L_f \text{ of ethanol} &: 1.04 \times 10^5 \text{ J kg}^{-1}\end{aligned}$$

Boiling - change of phase from liquid to vapour

- (i) at boiling point, there is no increase in temperature until all the liquid has vaporised even though heat, called the latent heat of vaporisation is being supplied to it.
- (ii) the latent heat of vaporisation is needed to
- separate the molecules further apart and allow them to move around independently as gas molecules,
 - enable the vapour to expand against the atmospheric pressure.
- (iii) latent heat of vaporisation is also regarded as increasing the potential energy of the molecules.

The specific latent heat of vaporisation L_v of a substance is defined as the quantity of heat required to change unit mass of the substance from the liquid state to its gaseous state without any change in temperature.

S I unit for L_v : J kg^{-1}

$$\begin{aligned}L_v \text{ for water} &: 2.26 \times 10^6 \text{ J kg}^{-1} \\L_v \text{ for ethanol} &: 8.54 \times 10^5 \text{ J kg}^{-1}\end{aligned}$$

The specific latent heat of vaporisation is higher than specific latent of fusion for the same substance.

(i) In boiling, molecules undergo large increase in intermolecular separation. On the other hand, upon melting the molecules undergo small increase in intermolecular separation. Therefore the increase in E_p is greater in boiling, i.e. more energy is needed to break the intermolecular bonds in boiling.

(ii) When boiling takes place, there is also large increase in volume as vapour occupies a larger volume than its liquid. When melting takes place, the increase in volume (sometimes even a small decrease as in water) is smaller. The work done against atmospheric pressure is greater when boiling occurs.

Therefore L_v is higher than L_f for the same substance.

Evaporation

Evaporation is the process by which a liquid, at any temperature, becomes a vapour.

This happens when the molecules near the liquid surface gain enough energy to overcome the attractive forces of the neighbouring molecules and thus able to escape from the liquid surface to the surroundings.

For a given external pressure, the evaporation rate increases with temperature, reaching a maximum rate at boiling point.

- Rate of evaporation depends on:

1. the temperature of the liquid,
2. the surface area of the liquid,
3. the nature of the liquid (volatile?),
4. the pressure above the surface of the liquid,
5. the movement of air above the surface of the liquid.

Cooling Effect Accompanies Evaporation

- According to kinetic model, at any temperature, the molecules of a liquid are in continuous random motion and making frequent collisions with each other.
- If a molecule which is near the surface of the liquid gains enough kinetic energy to do work against the attractive forces of the other molecules in the liquid and against the atmospheric pressure, then it is able to escape from the liquid to become a molecule of a vapour.
- Thus when a liquid evaporates, it loses the more energetic molecules, leaving those which are less energetic behind. Hence the average kinetic energy per molecule in the remaining liquid becomes lower. A liquid with molecules having a lower average kinetic energy has a lower temperature, therefore evaporation causes cooling.

Boiling

- happens throughout liquid body
occurs at a particular fixed temperature
external energy supply needed for change of state
- | | |
|-------------|---|
| Evaporation | 1. is a surface phenomenon |
| | 2. occurs at all temperatures |
| | 3. liquid cools because of loss of more energetic molecules |

Heat Capacity and Specific Heat Capacity

- When heat is supplied to an object, its temperature rises.

- The increase in temperature $\Delta\theta$ depends on Q , the amount of heat supplied and the mass m of the object.

$$\begin{aligned}\Delta\theta &\propto Q \quad \text{and} \quad \Delta\theta \propto 1/m \quad \Rightarrow \quad \Delta\theta \propto Q/m \\ &\Rightarrow Q \propto m(\Delta\theta) \\ &\Rightarrow Q = cm(\Delta\theta)\end{aligned}$$

$$Q = m c (\Delta\theta)$$

- Specific heat capacity c of a substance is defined as the quantity of heat required to produce unit rise of temperature in unit mass without a change of phase of the substance.

- S.I units for specific heat capacity are $J \text{ kg}^{-1} \text{ K}^{-1}$

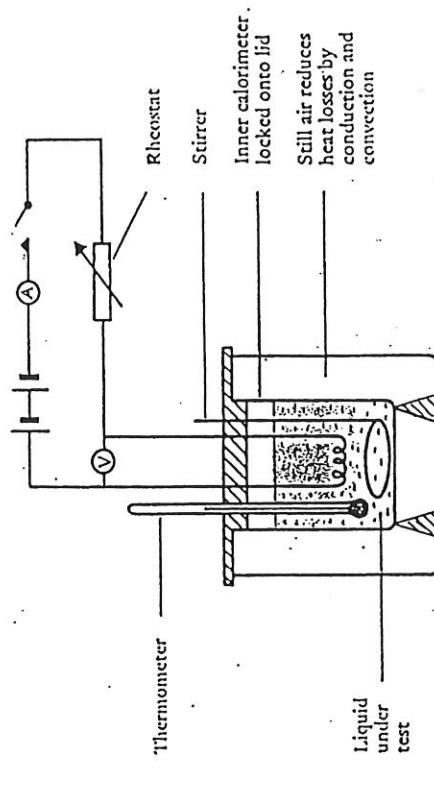
- Thus the heat needed to raise the temperature of a body of specific heat capacity c and mass m by $\Delta\theta$ is given by

$$\begin{aligned}Q &= m c (\Delta\theta) \\ \text{If } \theta \text{ increases, } \Delta\theta &\text{ is +ve} \Rightarrow Q \text{ is +ve (heat gain)} \\ \text{If } \theta \text{ decreases, } \Delta\theta &\text{ is -ve} \Rightarrow Q \text{ is -ve (heat loss).}\end{aligned}$$

- Heat capacity C of a body is defined as the quantity of heat required to produce unit temperature rise without a change of phase of the body.

- S.I unit of C : $J \text{ K}^{-1}$
- Amount of heat required to raise the temperature of a body by $\Delta\theta$ is $Q = C (\Delta\theta)$ as $C = m c$.

Determination of the Specific Heat Capacity of a Liquid



Molar heat capacity C_m is the heat required to raise the temperature of 1 mole of the substance by $1K$ without a change of phase of the substance

$$C_m = M C$$

$$= J \text{ mol}^{-1} \text{ K}^{-1}$$

$$C = s \cdot \theta$$

For n moles of a substance, $Q = n C_m \Delta T$

Steady State Condition

If the temperature of a conductor at any point does not change with time, the condition is called steady state.

Procedure is similar to that for solid except that liquid is stirred continuously during the heating.

Assuming no heat loss, by conservation of energy.

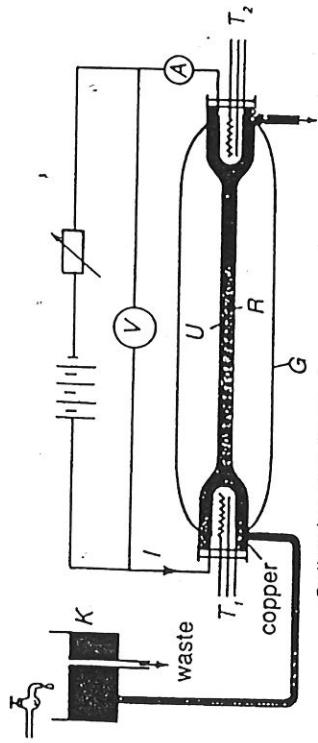
Energy supplied by heater = energy received by liquid + energy received by calorimeter & stirrer.

$$I_{Vt} = mc(T_f - T_i) + m_2 c_2 (T_f - T_i)$$

$$IVt = (m_c + m_2 c_2) (T_f - T_i)$$

Adjust rheostat to maximum constant current

Determination of the Specific Heat Capacity of a Liquid
(e.g. water) using the Continuous Flow Calorimeter



Callendar and Barnes' apparatus

- Water from a constant head tank K is passed through the glass tube U which contains a heating coil R.

- A current I (caused by a potential difference of V across R) is passed through the heating coil so that the liquid is heated as it is passed through the tube.

- Two platinum resistance thermometers T_1 and T_2 are used to measure the temperatures of the liquid before and after passing through the tube.

- The glass jacket G prevents heat loss from the liquid v conduction and convection.

- The liquid exiting the tube is collected and the total mass of liquid passing through the tube in time t is measured using a balance.

- The experiment is repeated with a different flow rate for the liquid and the current through R is adjusted until the thermometers show that the inlet and outlet liquid temperatures are the same as those in the first experiment. The liquid flow rate for the second experiment is also measured.

If heat loss neglected,

$$IV = \frac{m}{t} C (\theta_0 - \theta_i) \Rightarrow C = \frac{IVt}{(t)(\theta_0 - \theta_i)}$$

By conservation of energy,

Electrical energy supplied = heat gained by liquid + rate of heat loss per second

$$I_1 V_1 = \frac{m_1}{t_1} C (\theta_0 - \theta_{i1}) + h$$

$$I_2 V_2 = \frac{m_2}{t_2} C (\theta_0 - \theta_{i2}) + h$$

$$C = \frac{(I_1 V_1 - I_2 V_2)}{\left(\frac{m_1}{t_1} - \frac{m_2}{t_2}\right)(\theta_0 - \theta_i)}$$

The rate of heat loss to the surroundings is the same in both experiments as the temperature of the apparatus is kept the same for both experiments, hence can be accounted for.

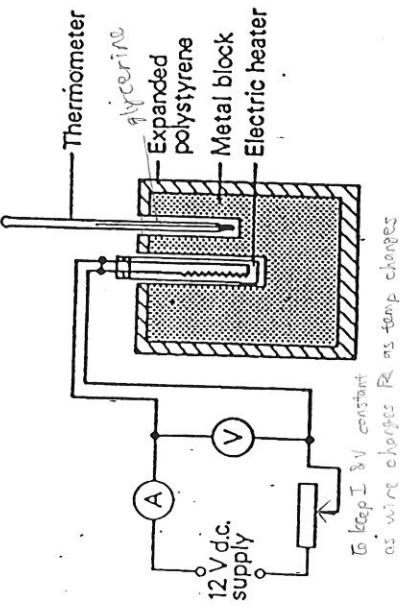
The constant head tank ensures a uniform flow rate of the liquid through the glass tube.

When steady state prevails, the heat supplied by the heating coil is all carried away by the liquid and is not taken in warming the apparatus since every part is at constant temperature. This means that the heat capacity of the apparatus is not required.

Determination of Specific Heat Capacity of a Solid

is recorded.

- By the principle of conservation of total energy,



This method is suitable for metals such as copper and aluminium that are good conductors of heat.

An electric heater which is connected to a d.c. supply is embedded in a cylindrical block of the material that is lagged with expanded polystyrene.

A thermometer is used to measure the temperature rise when a suitable steady current is switched on as a stopwatch is started.

The steady is maintained by adjusting the rheostat.

Glycerine is used to improve thermal contact between heater & the solid and thermometer & the solid.

The mass m of the block and the initial temperature θ_i is measured.

The block is then lagged with expanded polystyrene.

A suitable steady current is allowed to pass through the heating coil for a period of t seconds, and the readings of the ammeter and voltmeter taken and recorded as I and V

After switching off the heater, the final steady temperature θ_f

Heat supplied by the electrical heater = Heat gained by metal block

$$I^2 R t$$

$$IVt = m c (\theta_f - \theta_i)$$

Assumptions made:

readings are taken at steady state

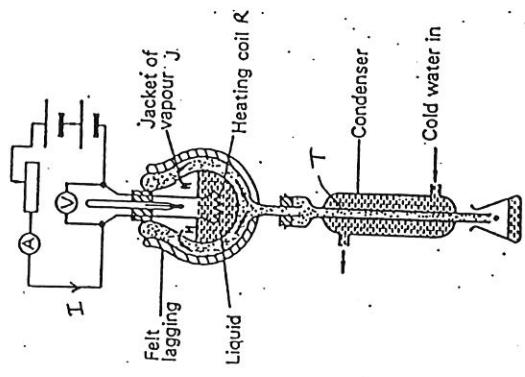
the small amount of heat absorbed by the thermometer and heater is neglected.

For more accurate result;

$$IVt = m c (\theta_f - \theta_i) + h$$

where h is the amount of heat loss.

Determination of Specific Latent Heat of Vaporisation



The electrical power = rate of latent heat + rate of heat loss

$$I_1 V_1 = \frac{m}{t_1} h + h$$

$$I_2 V_2 = \frac{m}{t_2} h + h$$

For more accurate results the experiment is performed twice with different heating rates, so that the rate of heat loss can be accounted for.

Let I_1 and I_2 be the currents for the 1st and 2nd experiments respectively.
 Let V_1 and V_2 be the voltage for the 1st and 2nd experiments respectively.
 Let m_1 and m_2 be the masses for the 1st and 2nd experiments respectively.
 Let t_1 and t_2 be the times for the 1st and 2nd experiments respectively.
 Let m_1 and m_2 be the masses for the 1st and 2nd experiments respectively.

$$h = \frac{(I_1 V_1 - I_2 V_2)}{\left(\frac{m_1}{t_1} - \frac{m_2}{t_2}\right)}$$

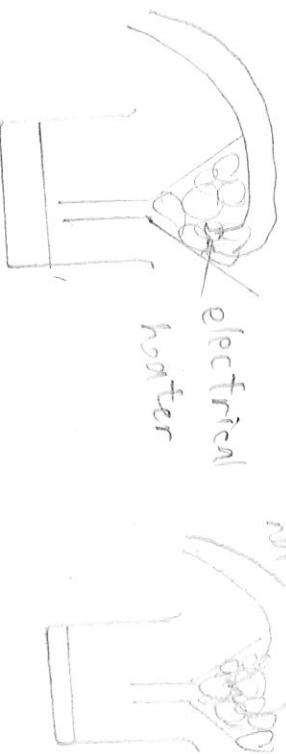
- The liquid under consideration is heated electrically by a coil R to boiling point.
- The vapour formed escapes through H into a surrounding jacket J and passes down the inner tube T of a condenser where it condenses and is converted to liquid by cold water flowing in the condenser.

- When a steady state is reached, the rate of vaporisation is equal to the rate of condensation.
- If the mass m of condensed liquid is collected in time t, then, By conservation of energy,

$$T V = \frac{m}{t} \Rightarrow h = \frac{IV}{\left(\frac{m}{t}\right)}$$

Determination of the specific latent heat of fusion of ice

in corrected



Electrical energy supplied by heater = heat needed to melt ice

$$\text{J} = \frac{(m_1 - m_2) \lambda}{t}$$

$$J_p =$$

The electrical heater is placed in a funnel containing some ice.

Beker placed below funnel to collect water from melting ice.

When heater is switched on, stopwatch is started

After a known interval of time t , heater is removed & mass of water measured.

During time heater is switched on, it's also absorb heat from surroundings

Assume no heat loss to container & surroundings
 heat lost by vegetables = heat gain + heat lost to warm up the water

Example 1
 1 kg of vegetables, having a specific heat capacity $2200 \text{ J kg}^{-1} \text{ K}^{-1}$, at a temperature of 373 K are plunged into a mixture containing some ice and 1 kg of water at 273 K . After all the ice has melted, the final temperature of the entire mixture is 300 K . Calculate the mass of ice originally present. Assume no heat loss to the container and the surroundings. [0.404 kg]

Example 2

Water flows at the rate of $0.1500 \text{ kg min}^{-1}$ through a tube and is heated by a heater dissipating at 25.2 W . The inflow and outflow temperatures are 15.5°C and 17.4°C respectively. When the rate of flow is increased to $0.2318 \text{ kg min}^{-1}$ and the rate of heating to 37.8 W , the inflow and outflow temperatures are unaltered. Find the rate of loss of heat from the tube. [2.1 W]

Example 3

A thermally insulated vessel containing liquid water and water vapour is connected to a vacuum pump which removes water vapour continuously. When the temperature reaches 0°C , the vessel contains 110 g of liquid water.

What mass of ice has been formed when no liquid remains?

Specific latent heat of fusion of water = $3.40 \times 10^5 \text{ J kg}^{-1}$,

Specific latent heat of vaporisation of water = $2.52 \times 10^6 \text{ J kg}^{-1}$ [0.097 kg]

internal energy of system \downarrow
 molecular E $\downarrow \Rightarrow$ temp \downarrow

m = mass of liquid water at 0°C , initially present in the container

$m_{\text{ice}} = \text{mass of ice formed when liquid remains}$

$$1(2200)(73) = m(3 - 3 \times 10^3) + (m+1)(4200)(300 - 273)$$

$$m = 0.404 \text{ kg}$$

$$\Sigma V = \left(\frac{m}{c}\right)(c)(\theta - \theta_i) + h$$

$$25.2 = \left(\frac{0.1500}{0.22318}\right)(c)(17.4 - 15.5) + h$$

$$37.8 = \left(\frac{0.2318}{0.50}\right)(c)(17.4 - 15.5) + h$$

Solving the equations, $h = 21 \text{ W}$

Heat absorbed by = Heat loss by water to large water to evaporate from liquid to solid (ice)

$$(m - m_{\text{ice}}) h_v = m_{\text{ice}} h$$

$$m_{\text{ice}} = \left(\frac{h_v}{h_v + h}\right) m$$

$$= \frac{2.52 \times 10^6}{(3.40 \times 10^5 + 2.52 \times 10^6)} (6.112)$$

$$= 0.097 \text{ kg}$$

$$= 97 \text{ g}$$

Thermodynamics deals with processes which cause energy changes as result of heat supplied to or taken from a system and/or work done on or by a system.

Heat and work are terms used to describe energy in transit.

Heat is the energy in the process of transfer between a system and its surroundings as a result of temperature differences only.

Work is energy that is transferred from one system to another by a force moving its point of application in its direction. $W = F \cdot S$

A thermodynamic system consists of a fixed mass of matter, often a gas, separated from its surroundings, perhaps by a cylinder and a piston.

The state of a system is specified by the values of certain experimentally measurable quantities called state properties.

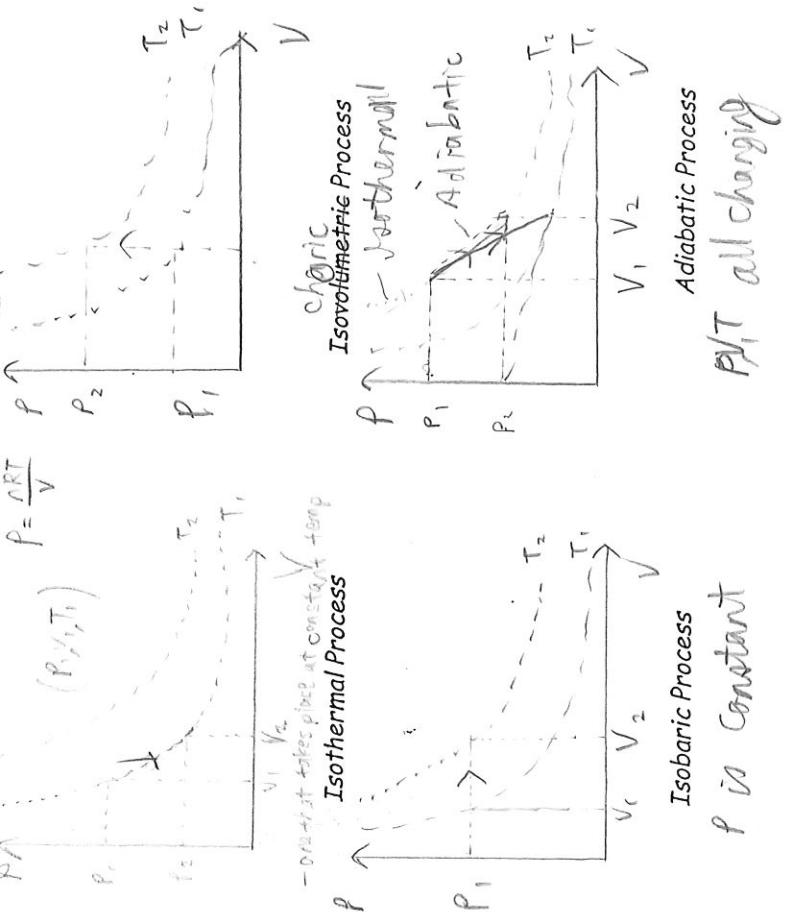
For example the state of a gas is completely specified by a knowledge of its pressure p, volume V, temperature T and amount (e.g. no. of moles).

A continuous change in the state of a gas is called a process.

A process in which the system is returned to its initial state is called a cycle.

Indicator Diagrams and Different Types of Processes

- When the pressure, volume and temperature of a gas change, it is useful to be able to show those changes on a graph.
- A single two-dimensional graph of pressure against volume graphs, each at different temperature, and then superimpose on these a line (with an arrow) to show how the state of a gas varies when certain changes are made.
- They are drawn for a fixed mass of gas.



$$c_f \cdot PV = nRT$$

First Law of Thermodynamics states that the increase in internal energy of a system is the sum of the heat supplied to the system and the work done on the system.

$$\text{Equation: } \Delta U = Q + W$$

The First law of thermodynamics is a restatement of the principle of conservation of energy.

When the above equation is used to represent the first law of thermodynamics, the following the sign convention is used.

Q is positive if heat is supplied to or absorbed by the system

Q is negative if heat is supplied by or given up by the system

W is positive if work is done on the system

W is negative if work is done by the system

ΔU is positive if there is a gain or increase in internal energy

ΔU is negative if there is a loss or decrease in internal energy

$$\Delta U = mC\Delta\theta$$

Internal Energy U

- Recall - the internal energy of a system is given by

$$U = E_k + E_p$$

- However for an ideal gas,

$$U = E_k$$

$$U = \frac{3}{2} nRT \quad \text{or} \quad U = \frac{3}{2} NkT \quad \Rightarrow \quad U \propto T$$

$$\Delta U = U_f - U_i \quad \Rightarrow \quad \Delta U \propto \Delta T$$

$$\Rightarrow \Delta U = 0 \quad \text{when } \Delta T = 0 \quad (\text{e.g. in a cyclic process})$$

- the internal energy is a function of the state of the gas, hence it does not depend on the path or process through the system is brought from its initial to its final states.
- $\Delta U = n C_m \Delta T$

ΔU
+ increase supplied on
 \rightarrow
- decrease given up by

$$\text{Work done} = p \Delta V$$

$$= 1.013 \times 10^5 (1671 - 1) 10^{-6}$$
$$= 169 \text{ J}$$

$$\Delta H = q + w$$

heat needed to vaporise kg of water to steam = mL

$$= (q)(2.256 \times 10^3) \text{ J g}^{-1}$$

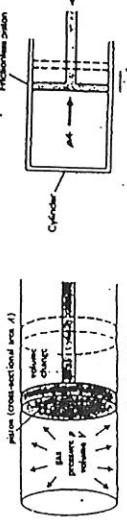
$$= 2.256 \times 10^3 \text{ J}$$

$$\Delta u = 2256 + (-169)$$
$$= 2087 \text{ J}$$

$$q = 2256 \text{ J}$$

heat supplied to gas = $\frac{W_d}{\text{gas}}$ by the gas
 internal energy = $\frac{W_d}{\text{gas}}$ of gas

Work Done By A Gas at Constant Pressure



Consider a gas contained in a cylinder by means of a frictionless movable piston of cross-sectional area A. Suppose that the pressure exerted by the gas at the piston face is p .
 The total force F exerted by the gas on the piston is pA .
 When the piston moves out an infinitesimal distance dx ,
 The work done dw by this force is given by

$$dw = F dx \Rightarrow dw = pA dx \Rightarrow dw = p dV$$

where $dV = Adx$ is the infinitesimal change of volume of the system.

For a finite change of volume from V_i to V_f , the total work done is $W = \int dw = \int p dV$

= area under a p vs V graph in the limit V_i & V_f

If the pressure p remains constant while the volume changes,
 The work done is given by $W = p \Delta V = p (V_f - V_i)$

Work done on the gas: (when the gas is compressed)

$$W_{\text{on}} = W = -P \Delta V \quad \text{where} \quad \Delta V = (V_f - V_i)$$

as $V_f < V_i$ and to follow sign convention where work done is taken to be positive hence the need for the negative sign.
 Work done by the gas: (when the gas expands)

$$W_{\text{by}} = -W_{\text{on}}$$

$$\text{if } T = \text{constant} \quad P = \frac{k}{V}$$

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{k}{V} dV$$

heat supplied = increase in internal energy of gas

increase in internal energy = heat supplied to gas + W_d by gas

$W_d = -W_{\text{on}}$ $- W_D = W_{\text{on}}$ used for 1st law

One gram of water become 1671 cm^3 of steam when boiled at a constant pressure of $1.013 \times 10^5 \text{ Pa}$. The specific latent heat of vapourisation at this pressure is $2.256 \times 10^6 \text{ J kg}^{-1}$. Calculate
 (a) the work done by the water when it vaporises;
 (b) its increase in internal energy.

[$169 \times 10^5 \text{ J}$; $2.09 \times 10^6 \text{ J}$]

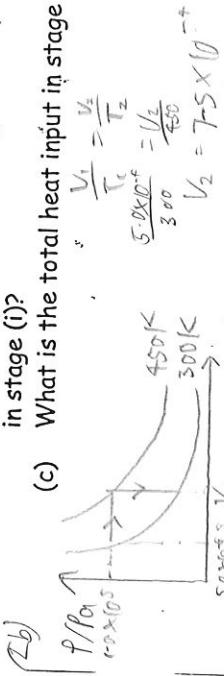
Example 2

A cylinder fitted with a frictionless piston contains an initial volume of $5.0 \times 10^{-4} \text{ m}^3$ of an ideal gas at a pressure of $1.0 \times 10^5 \text{ Pa}$ and a temperature of 300 K . The gas is heated at constant pressure to 450 K , and then
 (i) cooled at constant volume to the original temperature of 300 K .

The heat extracted from the gas during stage (ii) is 63 J .

- (a) Illustrate these changes on a p-V graph labeled with the appropriate values of pressure and volume.
 (b) How much work does the gas do in pushing back the piston in stage (i)?

[25 J] [88 J]



$$W_{\text{on gas}} = 1.0 \times 10^5 (7.5 - 5) \times 10^{-4} = -25 \text{ J}$$

$$W_{\text{on}} = 25 \text{ J}$$

$$\begin{aligned} \text{Thermal Properties/LI/MOH/22/0725} \\ \text{Thermal Properties/LI/MOH/22/0725} \\ \text{if } T = \text{constant} \quad P = \frac{k}{V} \\ W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{k}{V} dV \\ \Delta U = Q + W \\ = -63 + 0 = -63 \text{ J} \\ Q = 88 \text{ J} \end{aligned}$$

