TEMASEK JUNIOR COLLEGE

13 Thermodynamic Systems

Learning Outcomes

Students should be able to:

(a) show an understanding that the macroscopic state of a system determines the internal energy of the system, and that internal energy can be expressed as the sum of a random distribution of microscopic kinetic and potential energies associated with the particles of the system.

(b) show an understanding that the thermodynamic temperature of a system is (directly) proportional to the mean microscopic kinetic energy of particles.

(c) show an understanding that when two systems are placed in thermal contact, energy is transferred (by heating) from the system at higher temperature to the system at lower temperature, until they reach the same temperature and achieve thermal equilibrium (i.e. no net energy transfer).

(d) show an understanding of the difference between the work done by a gas and the work done on a gas, and calculate the work done by a gas in expanding against a constant external pressure: $W = p\Delta V$.

(e) recall and apply the zeroth law of thermodynamics that if two systems are both in thermal equilibrium with a third system, then they are also in thermal equilibrium with each other.

(f) recall and apply the first law of thermodynamics, $\Delta U = Q + W$, that the increase in internal energy of a system is equal to the sum of the energy transferred to the system by heating and the work done on the system.

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

1 Internal Energy

LO (a), (b)

We have seen from the previous topic that molecules of a **gas** possess *kinetic energies* due to their random motion. Not all molecules have the same kinetic energy because they are moving with different speeds, but the sum of all the kinetic energies will be a constant at that particular temperature.

For a **real gas**, because the molecules exert intermolecular *forces* on each other, there will be a certain *potential energy* due to the forces between the molecules and their positions relative to each other. Thus for a real gas, the internal energy is given by the sum of the potential energies and the kinetic energies of all the molecules.

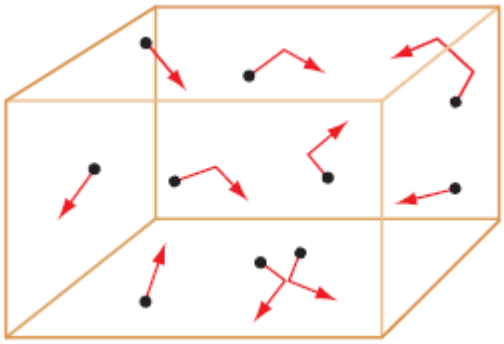


Fig. 3 The molecules of a gas have both kinetic and potential energies.

The internal energy *U*, of a system, is the sum of a random distribution of kinetic and potential energies associated with the molecules of a system**.**

$$U = \sum K.E._{microscopic} + \sum P.E._{microscopic}$$

Microscopic kinetic energy

- The microscopic KE arises from the continuous random motion of the particles.
- For monatomic gases, the microscopic KE refers to translational motion of atoms.
- For diatomic and polyatomic gases, the kinetic energies include other forms such as rotational and vibrational kinetic energies of the molecules.

> The **temperature** *T* of a gas is **a measure of the mean kinetic energy** of particles in the gas.

Microscopic potential energy

- The microscopic PE arises from the intermolecular forces and they depend on the type of bond between the particles and the intermolecular separation.
- Potential energy is the highest when the particles are separated far apart, and the potential energy drops as the particles are nearer. This is similar to gravitational potential energy: the potential energy is high when the object is high above the ground and low when the object is subjected to the gravitational attractive force and moves nearer to the ground.

Ideal Gas

For an **ideal gas**, there are **no intermolecular forces**. Therefore, the **potential energy** of the molecules is **zero**. The internal energy of an ideal gas is simply equal to the total kinetic energy of the molecules.

$$\text{internal energy of an ideal gas } U = \frac{3}{2}NkT = \frac{3}{2}nRT = \frac{3}{2}pV$$

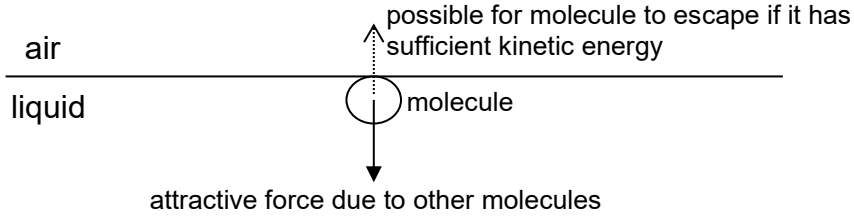
Note:

- U is proportional to the product NT or nT or pV.
- For a fixed amount of an **ideal gas**, $U \propto T$.

  When temperature changes by $\triangle T$, the change in internal energy, $\Delta U = \frac{3}{2}nR\Delta T$.

Evaporation

Evaporation is the process by which a liquid becomes vapour at **any** temperature. For a given external pressure, the evaporation rate increases with temperature, reaching a maximum at boiling point.



Due to the continual motion and collisions between the molecules in a liquid, their speeds change continually. Consider a molecule reaching the surface from within the liquid. If it has a kinetic energy large enough 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.

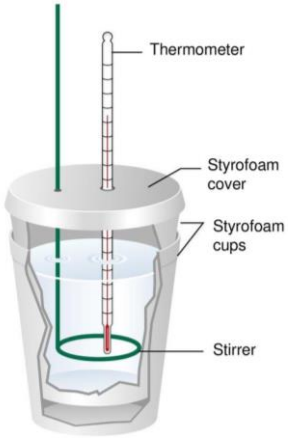
During evaporation, since molecules having larger kinetic energies escape, the average kinetic energy of the remaining molecules in the liquid decreases. Therefore the temperature drops and the liquid cools.

2 Temperature

2.1 Temperature and Heat

From the *macroscopic* perspective between systems, **temperature** is the physical property that determines the direction of heat flow. **Heat** then refers to the energy transferred between two systems at different temperatures. *Microscopically* however, we can define temperature as a measure of the **average kinetic energy** of molecules in a body.

2.2 Thermal Equilibrium *LO(c), (e)*



When two bodies of different temperatures are in **thermal contact**, net heat energy is transferred from the body at higher temperature to that at lower temperature. This heat transfer brings about a change in the microscopic kinetic and potential energies of the two bodies.

For instance, to measure the temperature of a cup of hot coffee, a thermometer is placed into the coffee. As the two bodies (hot coffee and thermometer) interact, the thermometer becomes hotter and the coffee cools off a little. After the thermometer settles down to a steady value, you read the temperature. The system of coffee and thermometer has reached an equilibrium, in which the interaction between the thermometer and the coffee causes no further change in the system. We call this a state of thermal equilibrium.

Two bodies in thermal contact are said to be in **thermal equilibrium** when there is no **net** flow of heat from one body to another. It also implies that the two bodies are at the same temperature.

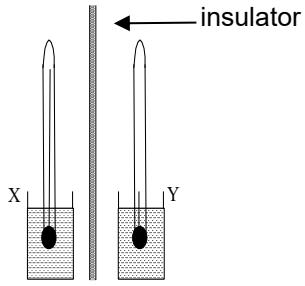


Fig. 1

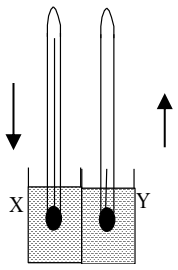


Fig. 2

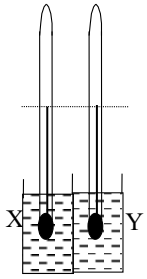


Fig. 3

Consider the two systems above, X and Y:

Fig 1: no thermal contact $\Rightarrow$ no flow of heat between X and Y.

Fig 2: X and Y in thermal contact. Since temperature of X > temperature of Y,
$\Rightarrow$ net heat flows from X to Y,
$\Rightarrow$ temperature of X decreases while that of Y increases.

Fig 3: X and Y in thermal equilibrium.
$\Rightarrow$ no **net** flow of heat between X and Y,
$\Rightarrow$ temperature of X = temperature of Y

Note: Heat cannot be stored. Heat refers to the energy transferred between two bodies at different temperatures.

Example 1

A solid X is in thermal equilibrium with a solid Y, which is at the same temperature as a third solid Z. The three bodies are of different materials and masses. Which one of the following statements is certainly true?

A It is not necessary that Y should be in thermal equilibrium with Z.
B It is not necessary that X should be at the same temperature as Z.
C There is no net transfer of energy if X is placed in thermal contact with Z

This shows the zeroth law of thermodynamics:

if two systems are both in thermal equilibrium with a third system, then they are also in thermal equilibrium with each other.

3 Thermodynamics

LO(f)

There are two obvious ways in which we can increase the internal energy of a gas: we can **heat** it, or we can do **work** on it.

***Q*:** Thermal energy or Heat *Q* is the energy transferred to the system by heating. For example, heat can be added by using another hot body such as using an electrical heater or a hot water bath.

***W*:** Work *W* is a transfer of energy by mechanical means, such as compressing the gas. For example, work can be done on a gas by a movable piston or using a bicycle pump.

Thermodynamics is the name given to the study of processes in which energy is transferred as heat and as work to a system.

3.1 First Law of Thermodynamics

We all know that energy is **conserved**. All the energy we put into a gas by heating it and by doing work on it must end up with an increase in the internal energy of the gas. This is stated in the First Law of Thermodynamics.

The first law of thermodynamics states that the increase in internal energy of a system is equal to the sum of energy transferred to the system by heating and the work done on the system.

Mathematically, it can be stated as

$$\Delta U = Q + W$$

ΔU = increase in internal energy = $U_{final} - U_{initial}$
Q = energy transferred to the system by heating
W = work done on the system

The sign conventions are:

ΔU is +ve if U ***increases***, ΔU is -ve if U ***decreases***

Q is +ve if energy is ***supplied to*** system by heating, Q is -ve if heat is ***removed from*** system

W is +ve if work is done ***on*** the system, W is -ve if work is done ***by*** the system

We can also replace W with W_{on} to remind ourselves that this term in the equation is the work done on the system, i.e.

$$\Delta U = Q + W_{on}$$

since the ***W*** in the equation is positive when work is done on the system.

The **internal energy of a system depends only on *the state of the system***.

The state of the system is defined by its pressure *p*, volume *V* and temperature *T*. It does not depend on the process or path through which the system is brought from its initial to its final state.

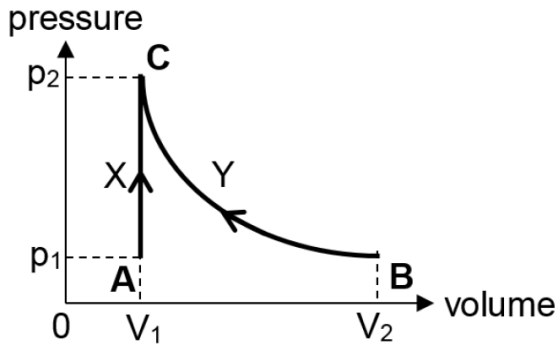
For example, if we regard all the gas in a cylinder to be the system, then the first law states that its internal energy only depends on factors such as the amount of gas in the cylinder, the pressure of the gas in the cylinder and its temperature. Another cylinder fills with same amount of gas under the same conditions, that is, in the same state, will have the same internal energy.

The P-V is a graph of *pressure versus volume* to illustrate the different processes a *fixed* mass of ideal gas can undergo. Each point **A**, **B**, and **C** on the graph represents the **state** of the gas described by its pressure *p*, volume *V* and temperature *T*.

Checkpoint:

The following ***p-V* diagram** (see diagram below) of a gas G is shown below. One mole of gas G was initially at state **A**. Gas G undergoes process X to reach state **C**. The internal energy of the gas G at state **C** is found to be U_C.

If one mole of the same gas, gas G, was initially at state **B** and undergoes process Y to reach state **C**, what will be the internal energy of the gas G at state C?



Answer: ***U_C***
The internal energy of a system depends only on *the state of the system*.
At state C, gas has the same P, V and T, therefore the same internal energy.

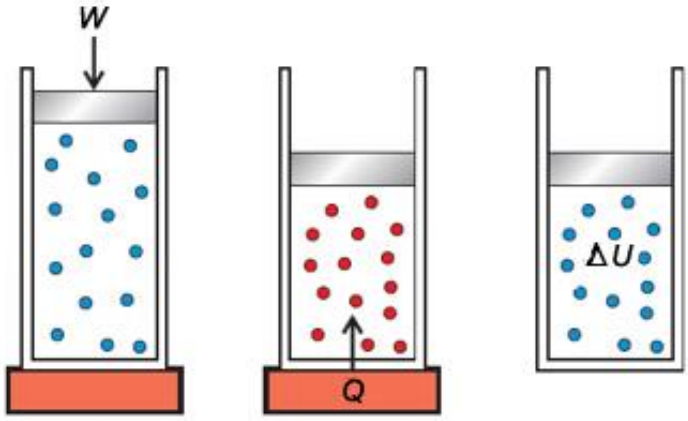
For change in Internal Energy:

If the system is an **ideal gas**,	If the system is **not** an ideal gas or *p*, *V* and *T* are not given, then use
Internal energy of ideal gas, U = E_K since E_P of ideal gas is 0. U = E_K = 3/2 nRT = 3/2 pV Change in internal energy, $\cdot \Delta U = 3/2\ nR\ (T_f - T_i)$ or $\cdot \Delta U = 3/2\ (P_fV_f - P_iV_i)$	$\Delta U = Q + W_{on}$

The first law of thermodynamics

The increase in internal energy of a system is equal to the sum of energy transferred to the system by heating and the work done on the system.

$$\Delta U = Q + W$$



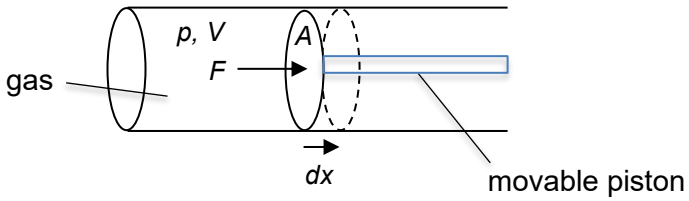
Example 2

Using the first law of thermodynamics, if 2500 J of energy is added to a system by heating, and 1800 J of work is done on the system, what is the change in internal energy of the system?

Solution:
The energy added to the system by heating Q = +2500 J
The work done on the system W_{on} = +1800 J
So from 1st law of thermodynamics, $\Delta U = Q + W_{on}$
$= 2500 + 1800 = 4300$ J

3.2 Work done by volume change *W* *LO(d)*

Consider a system, consisting of a fixed mass of gas, enclosed in a cylinder by a frictionless movable piston of cross-sectional area *A*.



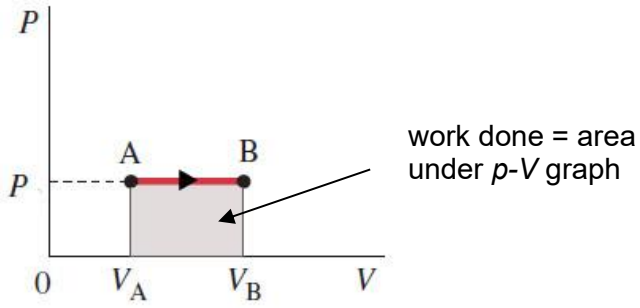
The gas is allowed to expand such that it pushes the piston to the right through a distance *dx* which is so small that the pressure *p* remains practically constant during the expansion.

Force exerted by the gas on the piston during expansion F = *pressure x area* = pA
Work done by the gas, dW_{by} = $F\,dx$
= $pA\,dx$
= $p\,dV$ where $dV = A\,dx$

In general, if the volume of the gas changes from V_i to V_f, the total work done by the gas is

$$W_{by} = \int_{V_i}^{V_f} p\,dV$$ = area under *p*-*V* graph

For example in the diagram, when a gas expands from A to B under constant pressure,



Work done by gas = area under p-V graph
= $p\,(V_B - V_A)$

During the expansion from A→B, work done by gas is +ve since V_B is larger than V_A.

Note that W_{on} and W_{by} are equal value but opposite signs.

i.e. $\boldsymbol{W_{on} = -W_{by}}$,

so work done on the gas $\boldsymbol{W_{on}}$ is –ve during expansion from A→B.

In general:

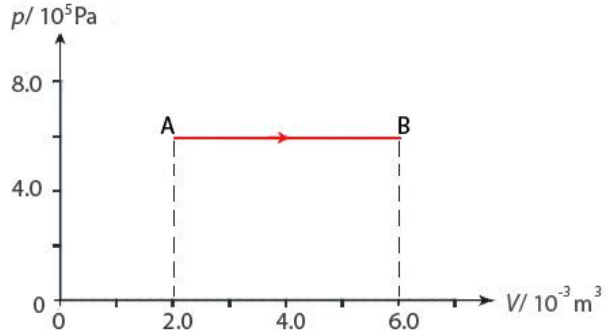
When a gas expands, work is done by the gas, so $\boldsymbol{W_{by}}$ **is +ve and** $\boldsymbol{W_{on}}$ **is –ve**.

When a gas is compressed, work is done on the gas, so $\boldsymbol{W_{by}}$ **is –ve** and $\boldsymbol{W_{on}}$ **is +ve.**

Example 3

In the following *p*-*V* diagrams, calculate the **work done on the gas from state A to B**.

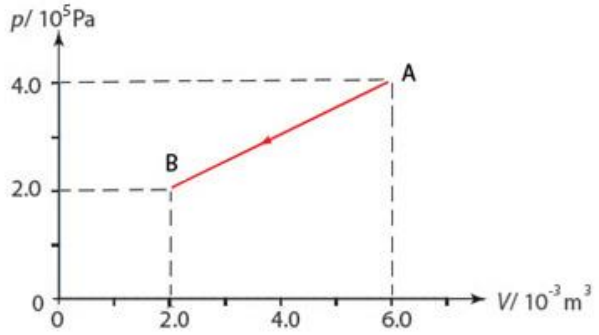
(a)



Solution:
Work done = area under *p*-*V* graph
$= 6.0 \times 10^5 \times (6.0-2.0)\times10^{-3}$
$= 2400$ J

Since the gas is expanding from A $\rightarrow$B, work is done ***by*** the gas, so
work done **on** the gas $W_{on} = -2400$ J

(b)



Solution:
Work done = area under *p*-*V* graph
$= \frac{1}{2}(2.0+4.0)\times10^5 \times(6.0-2.0)\times10^{-3}$
$= 1200$ J

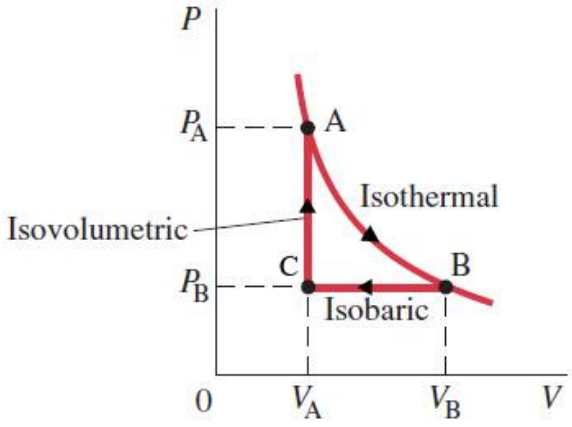
Since the gas is compressed from B$\rightarrow$A, work is done on the gas, so
work done **on** the gas $W_{on} = +1200$ J

3.3 *p*-*V* diagram

A ***p*-*V* diagram** (see diagram below) is a graph of *pressure versus volume* to illustrate the different processes a *fixed* mass of ideal gas can undergo. Each point **A**, **B**, and **C** on the graph represents the **state** of the gas described by its pressure *p*, volume *V* and temperature *T*.

The temperature *T* of each state can be calculated using the ideal gas equation $pV = nRT$ where *p* and *V* can be read from the graph and *n* is the amount of gas in moles.

Since **internal energy is determined by the state of the system,** the internal energies at A, B and C are different if their temperatures *T* (or the product *PV*) are different.



A **cycle** is a process during which a gas undergoes several changes but finally returns to its *original* state. In the figure shown, process A$\rightarrow$B$\rightarrow$C$\rightarrow$A is a cycle.

When a gas is brought round a complete cycle, there is no net change in internal energy.

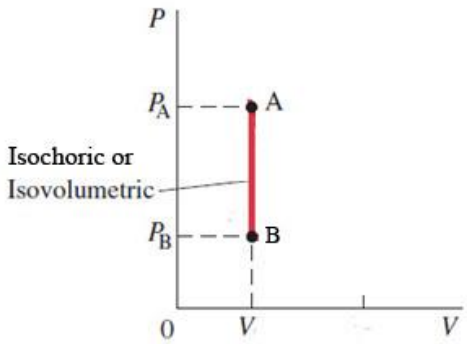
$$\Delta U = 0.$$

The net work done ***W*** = area enclosed by the cycle ABCA

3.4 Simple Thermodynamic Processes

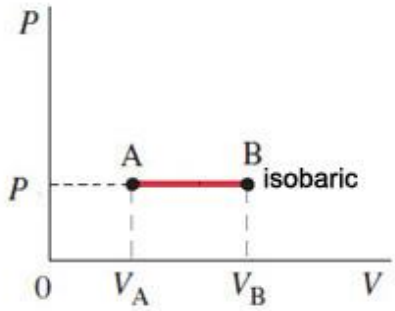
We shall discuss four simple thermodynamic processes that **an ideal gas** can undergo and apply the first law of thermodynamics to each process.

1. Isochoric (Isovolumetric) Process (constant volume process)



In isovolumetric or isochoric process,
volume is kept constant, $\Delta V = 0$
$\Rightarrow$Work done $\boxed{W = 0}$
Apply 1st law: $\Delta U = Q + W_{on}$
$= Q + 0$
$= Q$
$\Rightarrow$any heat Q added or extracted from system will result in ΔU. Since U changes, temperature T also changes.

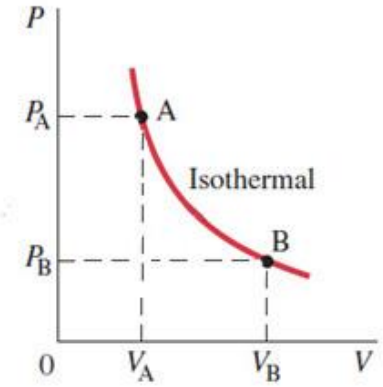
2. Isobaric Process (constant pressure process)



In isobaric process, pressure is kept constant.
Work done = area under p-V graph
$= P\Delta V = P(V_B - V_A)$
W_{on} is –ve during expansion from A$\rightarrow$B.
W_{on} is +ve during compression from B$\rightarrow$A.

Apply 1st law : $\Delta U = Q + W_{on}$, all terms are non-zero.

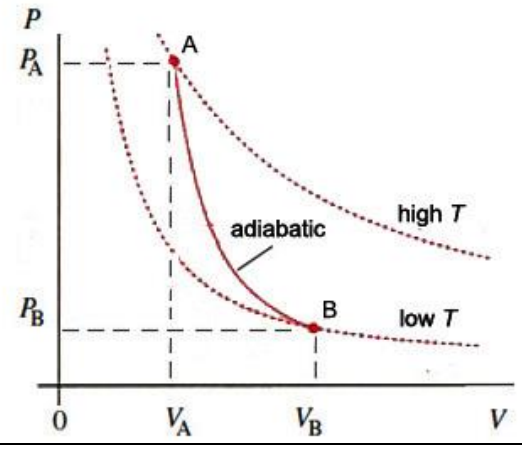
3. Isothermal Process (constant temperature process)



In isothermal process,
temperature is kept constant, $\Delta T = 0$.
hence no change in internal energy, i.e. $\boxed{\Delta U = 0}$

Work done W = area under p-V graph
Apply 1st law: $\Delta U = Q + W_{on}$
$0 = Q + W_{on}$
$\Rightarrow \quad Q = -W_{on} = W_{by}$
During isothermal expansion from A$\rightarrow$B, any heat Q added is converted to work done by the gas.
During isothermal compression from B$\rightarrow$A, heat Q extracted from system equals work done is on gas.

4. Adiabatic Process (Q = 0)



In adiabatic process, the system is very well-insulated or lagged, so that no heat can enter or leave the system, i.e.

$\boxed{Q = 0}$

Apply 1st law; $\Delta U = 0 + W_{on} = W_{on}$

In adiabatic expansion, W_{on} is –ve, so ΔU is –ve,
$\Rightarrow$ temperature decreases, gas cools

In adiabatic compression, W_{on} is +ve, so ΔU is +ve,
$\Rightarrow$ temperature increases, gas is hotter.

Example 4

A series of thermodynamic processes is shown in the *p*-*V* diagram below. In process A→B, 150 J of energy is added to the system by heating and in process B→C, 600 J of energy is added by heating.

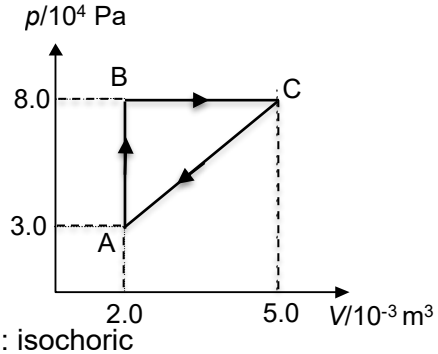
Calculate

(a) the internal energy change in the process A→B,

(b) the internal energy change in process B→C,

(c) the internal energy change in process C→A,

(d) the total energy added by heating in cyclic process A→B→C→A.



(a) Process A→B: isochoric

$\Delta V = 0 \Rightarrow W_{on} = 0$

Solution: $\Delta U_{AB} = Q + W_{on} = 150 + 0 = 150$ J

(b) Process B→C:isobaric

Work done on gas $W = -p\Delta V = -8.0 \times 10^4 \times (5.0 - 2.0) \times 10^{-3} = -240$ J

$\Delta U_{BC} = Q + W_{on}$

$= 600 + (-240)$

$= 360$ J

(c) In a cyclic process, net change in internal energy $\Delta U_{ABCA} = 0$

So $\Delta U_{AB} + \Delta U_{BC} + \Delta U_{CA} = 0$

$150 + 360 + \Delta U_{CA} = 0$

$\Rightarrow \Delta U_{CA} = -510$ J

(d) Work done on gas from C to A = area under line CA

$= \frac{1}{2}(3.0+8.0) \times 10^4 \times (5.0-2.0) \times 10^{-3}$

$= 165$ J

Net work done on gas from A→B→C→A, $W_{net} = W_{BC} + W_{CA}$

$= (-240) + 165$

$= -75$ J

= area enclosed by triangle ABCA

Apply the 1st law to the cyclic process,

$\Delta U_{ABCA} = Q_{net} + W_{net}$

$0 = Q_{net} + (-75)$

$Q_{net} = +75$ J

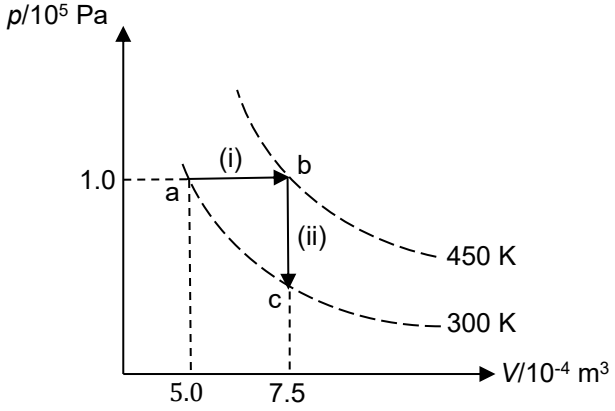
Example 5

A cylinder fitted with a frictionless piston contains an initial volume of 5.0×10^{-4} m^3 of an ideal gas at a pressure of 1.0×10^5 Pa and a temperature of 300 K. The gas is (i) heated at constant pressure to 450 K, then (ii) cooled at constant volume to the original temperature of 300 K. The heat extracted from the gas during stage (ii) is 38 J.

(a) Illustrate these changes on a *p*-*V* diagram.
(b) Calculate the work done by the gas in pushing back the piston in process (i).
(c) Calculate the heat gain in process (i).

Solution:

(a)



In stage (i), p is constant. So $V \alpha T$.

$$\frac{V_a}{V_b} = \frac{T_a}{T_b} \quad \Rightarrow \quad \frac{5.0 \times 10^{-4}}{V_b} = \frac{300}{450}$$

$V_b = 7.5 \times 10^{-4}$ m^3

(b) Work done *by* gas, $W_{ab} = p\,(V_f - V_i) = 1.0 \times 10^5\,(7.5 \times 10^{-4} - 5.0 \times 10^{-4}) = 25$ J

(c) ΔT in stage (i) = $-\Delta T$ in stage (ii)

Since, for an ideal gas, $\Delta U \ \alpha \ \Delta T$,

ΔU in stage (i) = $-\Delta U$ in stage (ii)
$Q_{ab} + W_{ab} = -(Q_{bc} + W_{bc})$
$Q_{ab} + (-25) = -(-38 + 0)$
$Q_{ab} = 63$ J

4.1 Specific Heat Capacity

LO (g)

When two different substances receive the same amount of energy they are not likely to undergo the same temperature change. The two substances are said to have different **heat capacities**.

Heat capacity of a body is defined as the **quantity of heat absorbed or liberated by the body per unit temperature change.**

That is,

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

where C is the heat capacity of the body, Q is the amount of heat and $\Delta\theta$ is the change in temperature. The S.I. unit for heat capacity is **J K^{-1}**.

For the same material, heat capacity varies with the mass of the body. A more useful quantity is the **specific heat capacity** which is the heat capacity per unit mass.

Specific heat capacity of a material is defined as the **quantity of heat absorbed or liberated per unit mass of the material per unit temperature change**.

That is,

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

where c is the specific heat capacity of the material, m is the mass of the material and $\Delta\theta$ is the change in temperature. The S.I. unit of specific heat capacity is **J kg^{-1} K^{-1}**.

Thus heat capacity = mass x specific heat capacity i.e. ***C = m c***

Example 6

An electric kettle contains 500 g of water at 15 °C. The heating element of the kettle is rated at 2.2 kW and the specific heat capacity of water is 4.2×10^3 J kg^{-1} K^{-1}.

(a) What is the heat capacity of the water in the kettle?
(b) What is the minimum time it takes to raise the temperature of the water to 100 °C.

Solution:

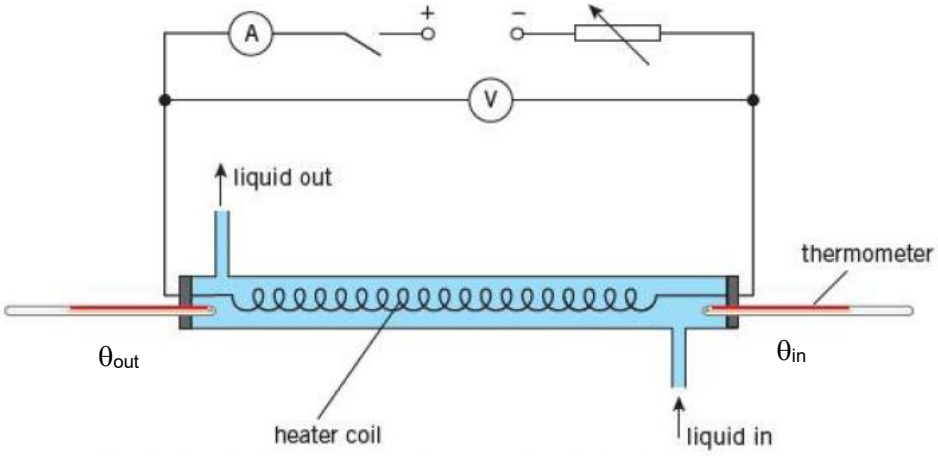
(a) heat capacity $C = m\,c$
$= 0.500 \times 4.2 \times 10^3$
$= 2.1 \times 10^3$ J K^{-1}

(b) Assume no heat loss to surroundings, the time t is the minimum time
heat supplied by the heating element = $C\,\Delta\theta$
$\Rightarrow \quad P\,t_{min} = C\,\Delta\theta$

$2.2 \times 10^3 \times t_{min} = 2.1 \times 10^3 \times (100 - 15)$
$t_{min} = 81$ s

Example 7

Water at 26.0 °C passes through a tube and is heated by a heating coil. The power supplied to the heating coil is 30.0 W. When water flows at a rate of 100 g min^{-1}, the temperature of the water leaving the end of the tube at steady state is 30.0 °C.



Another liquid at 26.0 °C is then passed through the same tube and to get the same change in temperature, the power is changed to 15.6 W and the rate of liquid flowing to 120 g min^{-1}. Calculate the specific heat capacity of the liquid if the specific heat capacity of water is assumed to be 4200 J kg^{-1} K^{-1}.

Solution:
By conservation of energy,

power supplied by heater	=	rate of heat gained by water/liquid	+	rate of heat loss to the surroundings

$$P = \frac{m}{t} c\Delta\theta + h$$ where h is rate of heat loss to the surroundings.

For water: $30.0 = \frac{0.100}{60} (4200) (30.0 - 26.0) + h$ ---------[1]

For liquid: $15.6 = \frac{0.120}{60} c (30.0 - 26.0) + h$ ---------[2]

Solving [1] and [2], $c = 1.7 \times 10^3$ J kg^{-1} K^{-1}

Question: Why is h the same in both cases?

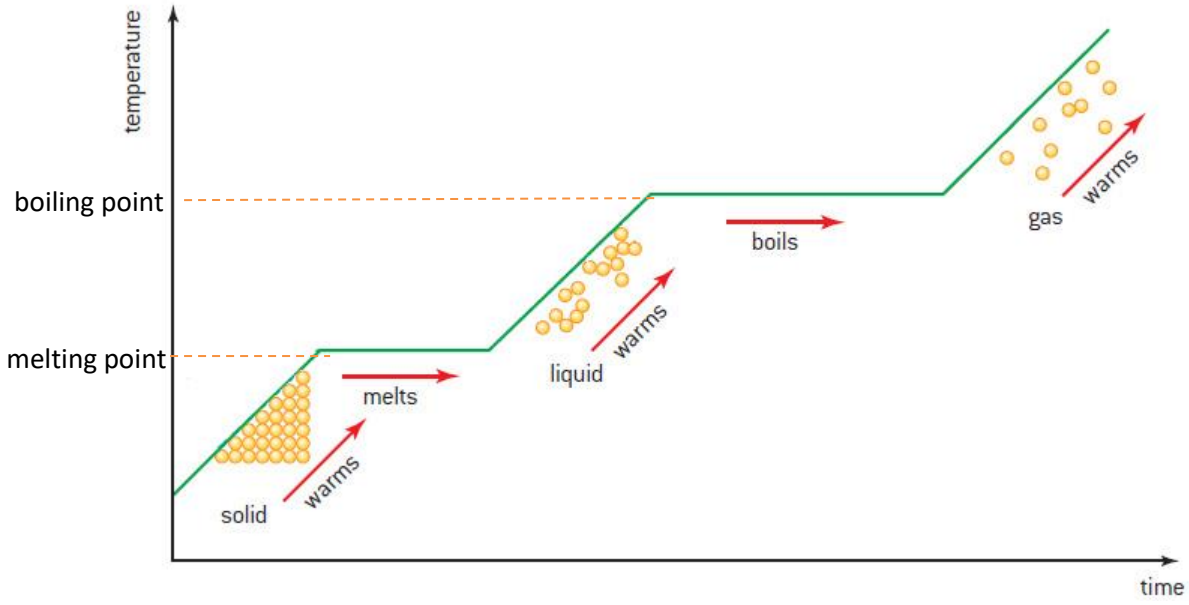
From *Newton's Law of Cooling*, the rate of heat lost from a body to the surroundings is proportional to its excess temperature over the surroundings.

By keeping the inlet and outlet temperatures of the tube constant in both cases, the excess temperature of the apparatus over the surroundings remain unchanged. Hence h is the same in both cases.

4.2 Specific Latent Heat

LO (g)

When heat is supplied at a constant rate to a substance, it undergoes a change of phase from solid to liquid to finally to gas or vapour as shown in the figure.



During the change in phase at melting point (solid→liquid) and at boiling point (liquid→gas/vapour), the thermal energy added does not cause the temperature to rise. The energy required to achieve the change of phase is called **latent heat**; the word *latent* meaning "hidden".

The latent energy of fusion supplied during melting is to break down the lattice structure, i.e. to break the intermolecular bonds of the solid.

The latent heat of vaporization supplied during boiling is to increase the intermolecular separation of the molecules and to do work as the gas expands against atmospheric pressure.

In both melting and boiling,

- the potential energies of the molecules are generally increased as the molecules are separated further apart.

- the total kinetic energies of the molecules are unchanged since temperature remains constant.

Latent heat is defined as the quantity of heat absorbed or liberated by a substance in order to change the substance from one phase to another phase without a temperature change.

The S.I. unit for latent heat is joule, **J**.

Specific latent heat of fusion of a substance is defined as the quantity of heat energy required to convert per unit mass of solid to liquid without a change in temperature.

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

where L_f is the specific latent heat of fusion and m is the mass of the substance.
The S.I. unit for specific latent heat of fusion is **J kg^{-1}**.

Specific latent heat of vaporisation of a substance is defined as the quantity of heat energy required to convert per unit mass of liquid to vapour without a change in temperature.

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

where L_v is the specific latent heat of vaporisation and m is the mass of the material.
The S.I. unit for specific latent heat of vaporisation is **J kg^{-1}**.

Note : Both *evaporation* and *boiling* represent a change of phase from liquid to vapour. However evaporation can take place at any temperature, whereas boiling takes place at a fixed temperature(boiling point). Furthermore evaporation takes place at the surface of the liquid, wheras boiling occurs in the body of the liquid.

The average kinetic energy of the molecules in the substance does not change during melting or boiling because the temperature of the substance remains unchanged during each process.

Example 8

Why is L_v higher than L_f for the same substance?
e.g. for ethanol, $L_v = 8.54 \times 10^5$ J kg^{-1} and $L_f = 1.04 \times 10^5$ J kg^{-1}

The increase in intermolecular separation is much greater during vaporisation than during melting.

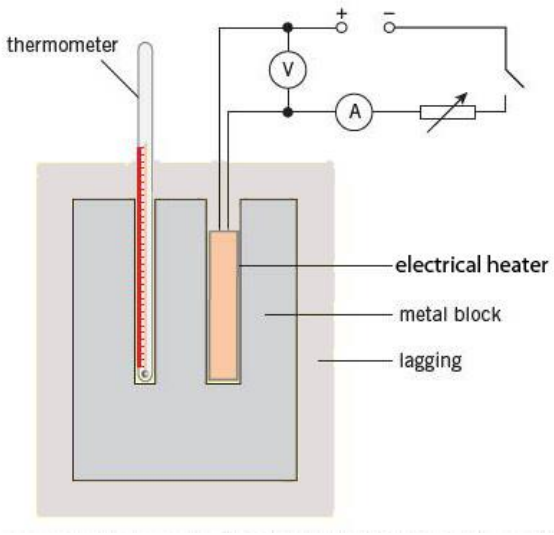
As such, the work done against the intermolecular forces is much larger. In addition, a small amount of work is done to overcome the atmospheric pressure as the vapour expands.

Therefore the specific latent heat of vaporisation is higher than specific latent heat of fusion.

Appendix

Determination of specific heat capacity of a solid

The specific heat capacity of a metal can be determined using a cylindrical block of the metal as shown in the Figure.



The mass *m* of the metal block is measured using a balance.

An electrical heater and a thermometer are inserted into holes in the metal block. The initial temperature θ_i is recorded.

The circuit is closed and the values of current *I* and p.d. *V* are noted. At time *t,* measured using a stopwatch, the final temperature θ_f is recorded.

Assuming no energy loss to the surroundings,

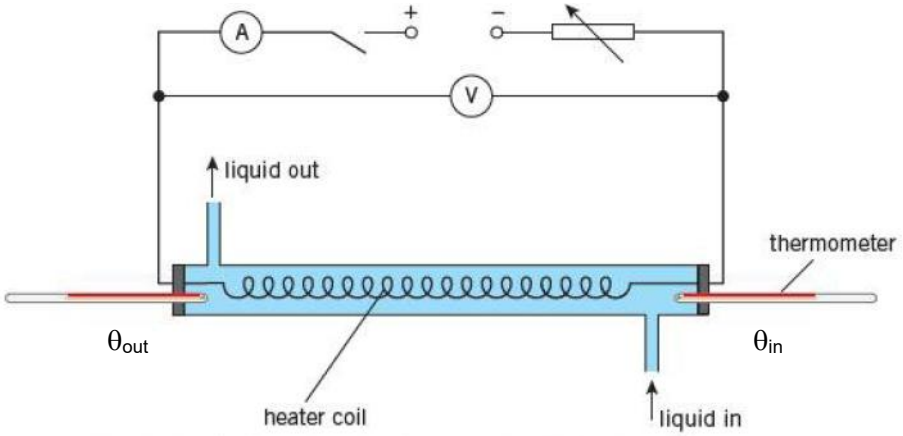
$$mc(\theta_f - \theta_i) = VIt$$

where c the specific heat capacity can be determined.

Question: If there is energy loss *H* to the surroundings due to poor lagging, what modification(s) should be made to the equation $mc(\theta_f - \theta_i) = VIt$?

Determination of specific heat capacity of a liquid

A reliable method for a liquid is based on continuous flow. The apparatus is as shown.



The liquid flows over the heater at a constant rate. When the inlet temperature θ_{in} and the outlet temperature θ_{out} are steady, the voltmeter reading V_1 and ammeter reading I_1 are recorded. The mass of liquid M_1 collected in time *t* is noted. Initially

Thermal energy supplied = thermal energy gained by liquid + energy losses to surroundings

$$V_1 I_1 t = M_1 c (\theta_{out} - \theta_{in}) + H$$

where c is the specific heat capacity and H is the thermal energy lost to the surroundings.

For the second set of readings, the temperatures are unaltered and therefore energy lost to the surroundings *H* is unchanged.

$$V_2 I_2 t = M_2 c (\theta_{out} - \theta_{in}) + H$$

Subtracting the two equations give

$$V_2 I_2 t - V_1 I_1 t = (M_2 - M_1) c (\theta_{out} - \theta_{in})$$

Hence thermal energy losses have been eliminated and c can be determined.

Supplementary Notes

What is the Second Law of Thermodynamics?

The First Law of Thermodynamics states that energy cannot be created or destroyed; the total *quantity* of energy in the universe stays the same. The Second Law of Thermodynamics is about the *quality* of energy. It states that as energy is transferred or transformed, more and more of it is wasted. The Second Law also states that there is a natural tendency of any isolated system to degenerate into a more disordered state.

Saibal Mitra, a professor of physics at Missouri State University, finds the Second Law to be the most interesting of the four laws of thermodynamics. “There are a number of ways to state the Second Law," he said. "At a very microscopic level, it simply says that if you have a system that is isolated, any natural process in that system progresses in the direction of increasing disorder, or entropy, of the system.”

All processes result in an increase in entropy. For example, crystals can form from a salt solution as the water is evaporated. Crystals are more orderly than salt molecules in solution; however, vaporized water is much more disorderly than liquid water. The process taken as a whole results in a net increase in disorder.

In practice, however, all exchanges of energy are subject to inefficiencies, such as friction and radiative heat loss, which increase the entropy of the system being observed. Therefore, because there is no such thing as a perfectly reversible process, if someone asks what is the direction of time, we can answer with confidence that time always flows in the direction of increasing entropy.

The Second Law indicates that thermodynamic processes, i.e., processes that involve the transfer or conversion of heat energy, are irreversible because they all result in an increase in entropy. Perhaps one of the most consequential implications of the Second Law, according to Mitra, is that it gives us the thermodynamic arrow of time.

Source: http://www.livescience.com/50941-second-law-thermodynamics.html

Tutorial Questions (Solutions are given for Questions 1, 5, 11 and 14.)

Internal Energy

1* (a) What do you understand by the *internal energy of a system*?
(b) State the physical quantities which affect the internal energy of any system.
(*1996/P3/Q5 part*)

Ans: *(a)* *Internal energy of a system is the sum of the kinetic energy of all the molecules due to their random motion and the potential energy of all the molecules due to their positions relative to each other and the forces between them.*

(b) *k.e. depends on Thermodynamic temperature T (or product PV), amount of substance n,*
p.e. depends on intermolecular forces and separation of molecules.

2 A substance changes from solid to liquid at its normal melting temperature. What change if any, occurs in the average kinetic energy and the average potential energy of its molecules?

	average kinetic energy	average potential energy
A	constant	constant
B	increases	constant
C	increases	decreases
D	constant	increases

First Law of Thermodynamics

3 (*2009/P1/Q21*) A fixed mass of ideal gas at high pressure is contained in a balloon. The balloon suddenly bursts, causing the gas to expand and cool. In this situation, which row describes the values of $\triangle U$, Q and W where $\triangle U = Q + W$, according to the first law of thermodynamics?

	$\triangle U$	Q	W
A	negative	negative	positive
B	negative	zero	negative
C	positive	zero	negative
D	positive	negative	positive

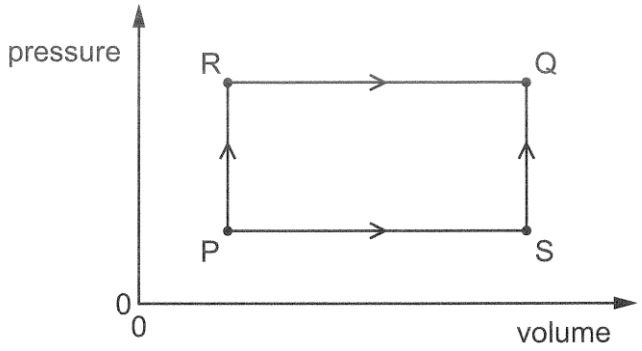
4 An ideal gas expands isothermally, doing 250 J of work.
(a) What is the change in internal energy?
(b) How much thermal energy is absorbed in the process?

[0 J, 250 J]

5* Use the first law of thermodynamics to explain the change, if any, in the internal energy
(a) of the water in an ice cube when the ice melts, at atmospheric pressure, to form a liquid without any change of temperature,
(b) of the gas in a tyre when the tyre bursts so that the gas suddenly increases in volume. Assume that the gas is ideal.

Solution:
(a) volume decreases from ice to water, so work done on the system. However this small volume change so work done on system si negligible ($W \approx 0$)
thermal) energy absorbed to break lattice structure of ice (Q is +ve)
so internal energy increases
(b) gas expands so work done by gas (against atmosphere) (W is -ve)
no time for thermal energy to enter or leave the gas ($Q \approx 0$)
so internal energy decreases

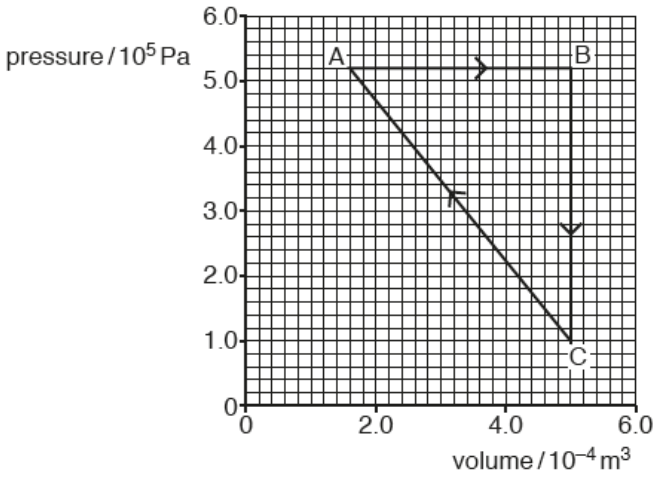
6 *(2016/P1/Q19)* A fixed mass of gas undergoes changes of pressure and volume as shown.



When the gas is taken from state P to state Q by the stages PR and RQ, 3 J of work is done by it and there is a thermal transfer of 8 J of energy into it.

When the same resultant change is achieved by stages PS and SQ, 1 J of work is done by the gas. In this case, what is the thermal transfer of energy? [Q = +6 J]

7 A fixed mass of an ideal gas undergoes a cycle ABCA of changes, as shown in the figure.



(a) During the change from A to B, the energy supplied to the gas by heating is 442 J. Use the first law of thermodynamics to calculate the increase in internal energy of the gas

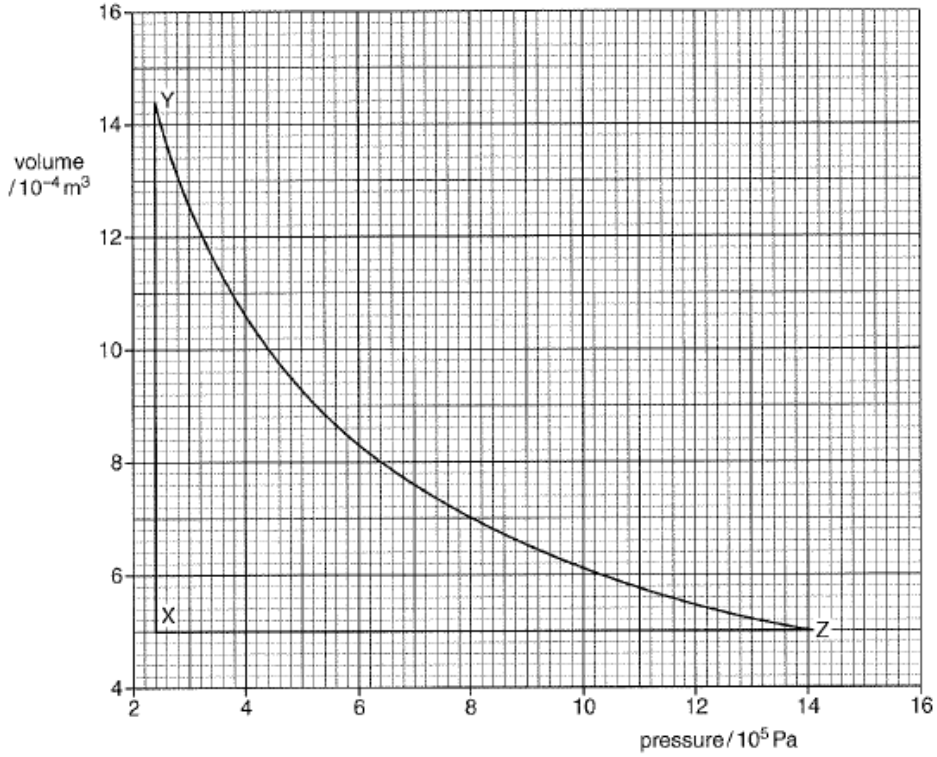
(b) During the change from B to C, the energy extracted from the gas is 313 J. Calculate the change in internal energy of the gas.

(c) Calculate the change in internal energy for the change from C to A.

(d) Calculate the net work done by the gas during the cycle ABCA.

[265 J, -313 J, +48 J, 71J]

8 (*2014/P3/Q3*) A fixed mass of an ideal gas undergoes the cycle of changes XYZX as shown.



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

(a) Calculate the amount of gas.

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

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

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

(c) Some energy changes during one cycle XYZX are shown in the table. Use your answers to (b) to complete the table.

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

[0.050 mol, 226 J]

9. (*N2022P3Q2*) At room temperature, a metal wire is connected to a d.c. power supply. When the power supply is first switched on, the wire heats up from room temperature to a higher constant temperature in a time of 60 s.

(i) The first law of thermodynamics, when applied to the system, can be expressed as

$$\Delta U = Q + W$$

where ΔU is the increase in internal energy of the system,
Q is the heat supplied to the system, and
W is the work done on the system.

Use words **positive**, **negative** and **zero** to complete the table below for the first three terms in the equation for the wire at the times shown. You may use each word once, more than once or not at all.

time after being switched on	ΔU	Q	W
0 – 59 s			
60 – 100 s			

(ii) At its higher constant temperature, the current in the wire is 12 A and the potential difference across it is 230 V.

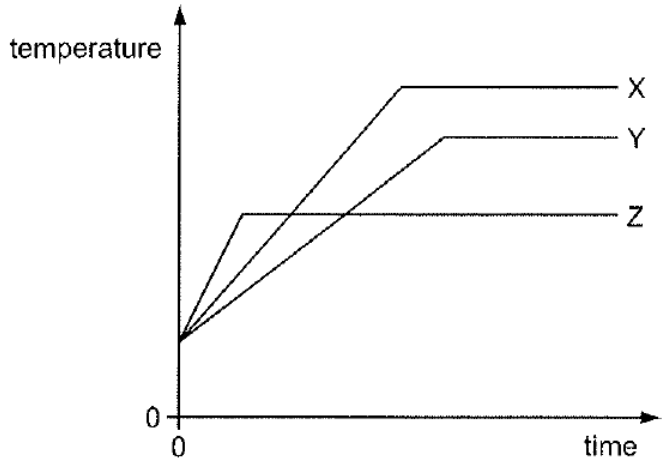
Complete the table below to show the values of ΔU, Q and W for a time of 40 s at this higher constant temperature.

ΔU/J	Q/J	W/J

Specific Heat Capacity and Specific Latent Heat

10. An ice cube of mass 25.0 g and temperature 0.0 °C is dropped into a glass of water of mass 300 g and initial temperature 20.0 °C. What is the final temperature of the mixture? Given specific heat capacity of water = 4200 $Jkg^{-1}\ K^{-1}$;
specific latent heat of fusion of ice = 334000 Jkg^{-1}. [12.3 °C]

11* (*2014/P1/Q18*) Equal masses of three liquids X, Y and Z are heated from room temperature.



Energy is supplied by heating at the same rate to each liquid. The graph shows how the temperature of each liquid varies with time after heating starts.

Which liquid X, Y or Z has the largest specific heat capacity?

Solution: *Since Power supplied* $P = mc\,\frac{d\theta}{dt}$

For the same mass m and same power P supplied, $c \propto \frac{1}{\frac{d\theta}{dt}}$ *where* $\frac{d\theta}{dt}$ *is the gradient*

From graph, Y has the least gradient $\frac{d\theta}{dt}$*, so its c is the largest.*

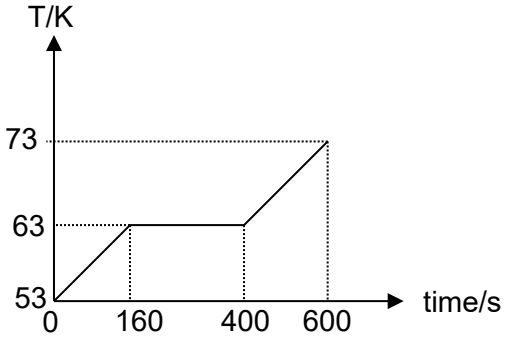
12 (*2010/P3/Q1*) A student carries out an experiment to determine the specific latent heat of vaporisation of water. Water is boiled in a beaker by means of an electric heater. The power *P* supplied to the heater is measured. When the water is boiling at a constant rate, the mass *m* of water evaporated in 5.0 minutes is determined. Data for the power *P* and the mass m for two different values of *P* are shown in the table.

P / W	*m* / g
140	14.1
95	8.2

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

(b) Calculate the value for the specific latent heat *L* of vaporisation. [2.29×10^6 J kg^{-1}]

13 The graph refers to an experiment in which an initially solid specimen of nitrogen absorbs heat at a constant rate. Nitrogen melts at 63 K and the specific heat capacity of solid nitrogen is 1.6×10^3 J kg^{-1} K^{-1}.



Assume no heat losses.

(a) Calculate the specific latent heat of fusion of nitrogen.
(b) Calculate the specific heat capacity of liquid nitrogen.

[2.4×10^4 J kg^{-1}, 2.0×10^3 J kg^{-1}K^{-1}]

14* Explain why the *latent heat of vaporisation* is greater than *latent heat of fusion* for the same substance. (e.g. for ethanol, $L_v = 8.54 \times 10^5$ J kg^{-1} and $L_f = 1.04 \times 10^5$ J kg^{-1})

Solution:
The energy required to completely separate the molecules from liquid state to vapour state is much greater than the energy required to break the lattice structure/rigid bonds of solid to become liquid. Furthermore energy must be provided to push back the atmosphere as the liquid turns into vapour since the volume of vapour is much greater than the volume of the liquid.
Therefore the specific latent heat of vaporisation is greater than specific latent heat of fusion.