13 THERMODYNAMIC SYSTEMS

H2 Physics 9478

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Learning Outcomes

Candidates 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 use 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 heat supplied to the system and the work done on the system.

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

Thermodynamic Systems – An Overview

The first law of thermodynamics is central to understanding thermodynamic processes which involve heat transfer and mechanical work. This law is an extension of the conservation of energy used in mechanics as it considers energy exchange in a system by means of both heat transfer and mechanical work.

Through the ways which energy can be transferred between a system and its surroundings, changes in the internal energy of the system can result. The concept of internal energy is introduced to make the link between heat and mechanical work to measurable macroscopic properties like pressure, volume and temperature. This internal energy is also related to microscopic kinetic and potential energies associated with the particles of the system.

Linking the ideas about heat and temperature is the zeroth law of thermodynamics, which states that when two objects at different temperature are placed in thermal contact, there will be energy exchange between them until thermal equilibrium is reached. The zeroth law allows the use of thermometers to measure temperature. When thermal equilibrium is achieved, the thermometer reflects its own temperature which is of the same value as the other body that it is in thermal contact with.

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

13.1 Internal Energy

❖ Properties of molecules in different phases

Matter is made up of a large number of molecules, which are particles whose dimensions are about 10^{-10} m. Evidence for the existence of molecules is given by experiments demonstrating Brownian motion (refer to Appendix in Chapter 12).

There are three phases of matter: solid, liquid and gas. **Table 13.1** is a summary of their characteristics and shows the difference between the phases.

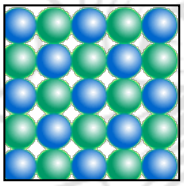
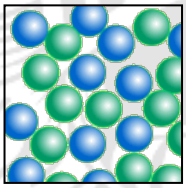
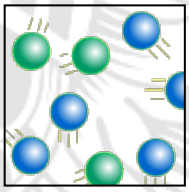
	Solid	**Liquid**	**Gas**
Packing arrangement of atoms/ molecules	Atoms / molecules are closely packed in a regular pattern called a lattice structure (regular, geometrical structure)	Atoms / molecules are slightly further apart than in solids	Atoms / molecules are significantly further apart
Illustration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

Table 13.1

❖ Microscopic kinetic energy

The microscopic kinetic energy (KE) of a body is due to the kinetic energies of its particles due to their constant random motion, which can be translational, rotational or vibrational as shown in Fig. 13.1.

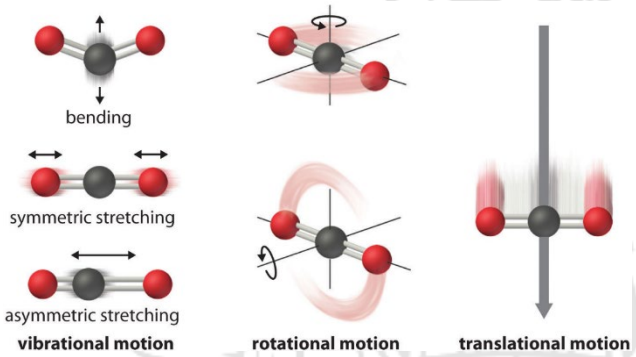


Fig. 13.1

In a body, there is a large number of particles in it (one mole contains 6.02×10^{23} particles), and each particle has its own individual microscopic KE. It is usually not meaningful to consider individual particle's microscopic KE, hence we consider their average microscopic KE instead.

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

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

❖ Microscopic potential energy

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

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

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

❖ Internal energy of a system

The state of a system can be described by its state variables, namely its pressure, volume, number of moles, and temperature. The internal energy of the system is determined by the state of this system.

We can relate the internal energy (macroscopic property) to the KE and PE of the molecules (microscopic properties) in a body or system.

Singapore's Energy Story

Definition of Internal Energy of a System

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

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

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

Singapore's Energy Statistics

❖ Relationship between temperature and internal energy

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

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

❖ Internal energy of an ideal gas

Recall that for a monatomic ideal gas, the microscopic kinetic energy is directly proportional to its absolute temperature T (derivation in Chapter 12.3).

For **one** molecule:

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

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

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

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

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

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

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

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

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

We see that ΔU is solely dependent on the change in thermodynamic temperature ΔT, and only a change in the product of pV which results in a change in T will result in a change in internal energy ΔU.

Note

- $\Delta U = \frac{3}{2} \Delta (pV) = \frac{3}{2} [p_f V_f - p_i V_i]$

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

- The factor of $\frac{3}{2}$ applies only to monatomic gases, i.e., gases made up of single atoms. Such atoms perform **translational** motion only.
- For this reason, $\frac{3}{2}kT$ is sometimes referred to as the mean **translational** kinetic energy.
- For non-monatomic molecules,
  - the molecules now have rotational and vibrational motion, in addition to the **translational** kinetic energy.
  - Hence, $\frac{3}{2}kT$ **does not apply.**
  - In this case, it is safer to analyse the ideal gas system using the First Law of Thermodynamics, which will be discussed in the section **13.3**.

Example 13.1

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

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

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

13.2 Heating and Work Done

❖ Thermal equilibrium

When heat can be exchanged between, the objects are said to be in **thermal contact**. For two objects in thermal contact, the object at the higher initial temperature loses heat and its temperature decreases whereas the object at the lower initial temperature gains heat and its temperature increases.

Some time later, net heat transfer between them ceases i.e. each object gains heat from and loses heat to the other object at the same rate. The two objects are said to be in a state of ***thermal equilibrium***.

Definition of Thermal Equilibrium

When there is **no net flow of heat** between two objects in thermal contact, the two objects are in a state of ***thermal equilibrium***.

This implies that the **temperatures** of the two objects are equal. For example, a hot cup of coffee left in a room will eventually cool as thermal equilibrium is attained between the cup of coffee and its surroundings and both will be at the same temperature.

Two objects are in thermal equilibrium if and only if they are at the same temperature. Hence temperature can be thought of as the property that determines whether an object is in thermal equilibrium with other objects.

❖ Work done

Consider a system of gas in a cylinder with a frictionless, movable piston of cross-sectional area *A* in contact with the gas. When the gas **expands**, a force *F* is applied on the piston **by** the gas to move the piston against the external pressure as shown in Fig. 13.2.

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

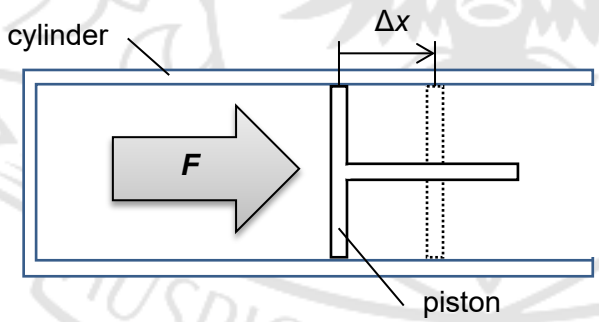


Fig. 13.2

The work done by this force *F* in displacing the piston through a small distance *dx* against the external pressure *p* is known as **positive work done <u>by</u> the gas**. This results in a change in volume $\Delta V = A\Delta x$.

Work done by the gas,

$$W_{\text{by gas}} = F\,\Delta x$$
$$= (pA)\Delta x = p(A\,\Delta x)$$
$$\therefore \boxed{W_{\text{by gas}} = p\,\Delta V}$$

Therefore, the work done on the gas,

$$\boxed{W = -p\,\Delta V}$$

If the gas is compressed, ΔV is negative and work done on the gas is positive. If the gas expands, ΔV is positive and work done on the gas is negative.

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

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

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

13.3 Laws of Thermodynamics

❖ Zeroth law of thermodynamics

The concept of objects in thermal equilibrium being at the same temperature is formalised in the Zeroth Law of Thermodynamics which can be stated as follows:

Definition of Zeroth Law of Thermodynamics

If objects A and B are each separately in thermal equilibrium with a third object C, then A and B are also in thermal equilibrium with each other.

A and C are in thermal equilibrium B and C are in thermal equilibrium

then A and B are also in thermal equilibrium

In summary, if $T_A = T_C$ and $T_B = T_C$, then $T_A = T_B$, where T_A, T_B and T_C are the temperatures of objects A, B and C respectively.

One may use object C as a **thermometer** to measure the temperatures of objects A and B separately. If the results of the two separate measurements yield the same value for objects A and B, then it can be inferred that they will be in thermal equilibrium with each other if they are to be brought into thermal contact i.e. there will not be any net heat transfer between them as their temperatures are the same.

The importance of this law was recognised only after the first and second laws of thermodynamics had been established. Since it is most fundamental, the name "zeroth" seemed appropriate.

❖ First Law of Thermodynamics

The principle of conservation of energy states that the total energy of an isolated system remains constant, and that energy can neither be created nor destroyed but can only be transferred from one store to another.

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

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

Definition of First Law of Thermodynamics

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

Word equation form:

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

Mathematical equation form:

$$\Delta U = Q + W$$

Sign Conventions

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

Hence if any of the quantities are calculated or defined as negative, it just means the opposite of how it was defined in the First Law.

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

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

❖ Pressure-Volume Graphs

All states of an ideal gas can be represented on a *p*-*V*-*T* surface as shown in Fig. 13.3.

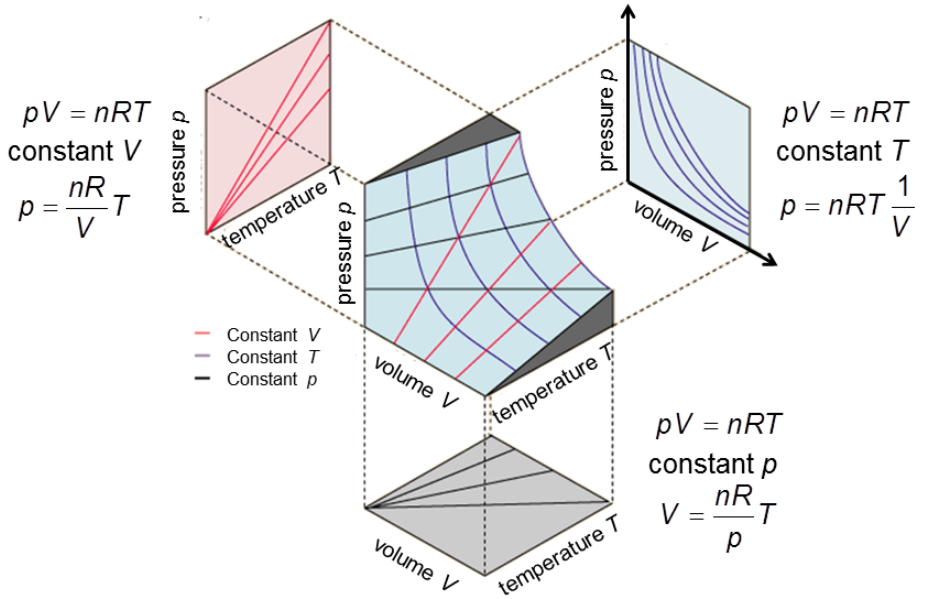
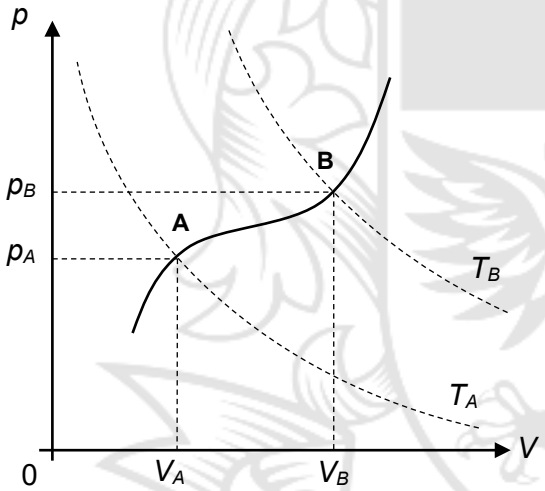


Fig. 13.3

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

❖ Information from a *p*-*V* diagram



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

(1) Pressure changes from p_A to p_B

(2) Volume changes from V_A to V_B

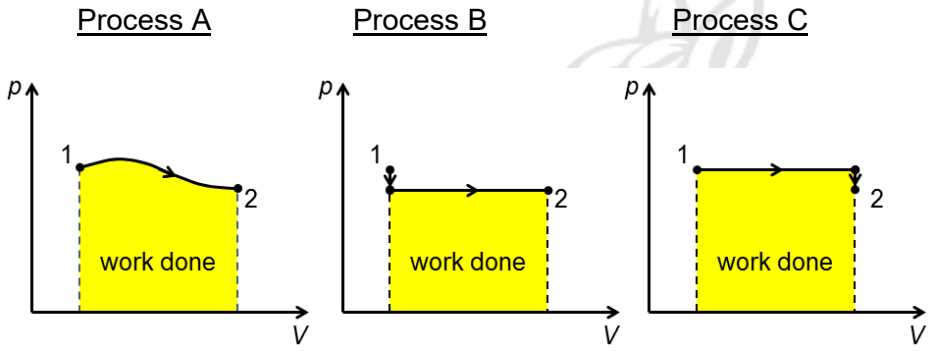
(3) This implies a temperature change from T_A to T_B

(4) Thus, there is a **change** in internal energy from U_A to U_B,

where the **increase** in internal energy is $\Delta U = U_B - U_A$

❖ Internal Energy *U* & Work done *W*

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



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

- For all three processes A, B and C, the gas changes from state 1 to state 2.

  $\therefore \Delta U = U_2 - U_1$, is the same for all three processes.

- Work done *W* = area under the *p*-*V* graph

  Based on the areas shaded, $|W_B| < |W_A| < |W_C|$

In summary,

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

❖ Special Processes

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

(1) Constant Temperature (Isothermal)

(2) Constant Pressure (Isobaric)

(3) Constant Volume (Isovolumetric / Isochoric / Isometric)

(4) No Heat Transfer (Adiabatic, $Q = 0$)

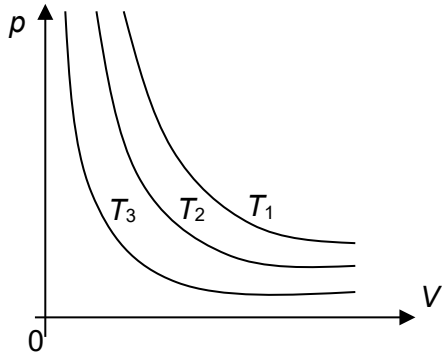
(5) Cyclic Process

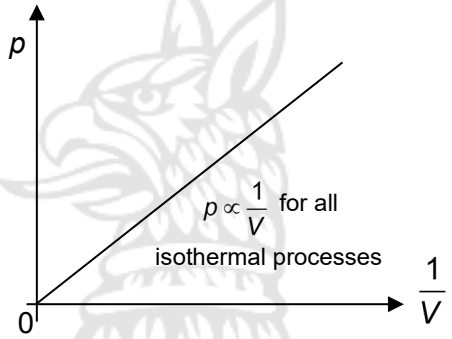
(1) Constant Temperature (Isothermal)

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

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

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

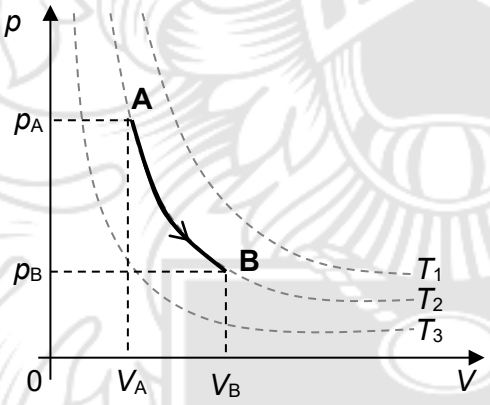




As temperature T increases, (nRT) increases, and the plot of p-V shifts upwards.

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

<u>Isothermal Expansion</u>



In any expansion, volume increases,

- Work done **ON** the system, W is <u>*negative*</u>

Temperature remains the same from A to B

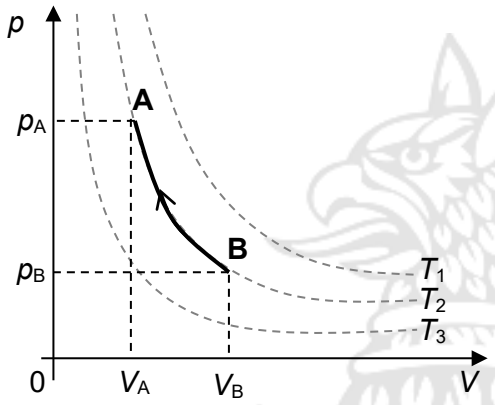
- Internal energy remains the same, $\Delta U = 0$

Process	Q	W	ΔU
A to B	+	–	0

By the 1st Law of Thermodynamics:

Since $\Delta U = 0$, $\quad Q = -W$

Isothermal Compression



In any compression, volume decreases,

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

Temperature remains the same from B to A

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

Process	Q	W	ΔU
B to A	–	+	0

By the 1st Law of Thermodynamics:

Since $\Delta U = 0$, $\quad Q = -W$

(2) Constant Pressure (Isobaric)

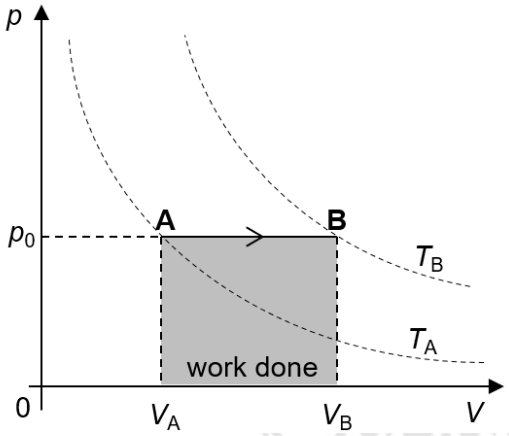
If the gas undergoes heat exchange such that its volume change occurs at constant pressure, the process is known as an *isobaric* process (*bar* is a unit of pressure). The area under the p-V graph is rectangular and the magnitude of the work done is thus $p\Delta V$.

Work done on a gas

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

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

Isobaric Expansion



In any expansion, volume increases,

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

Temperature increases from A to B

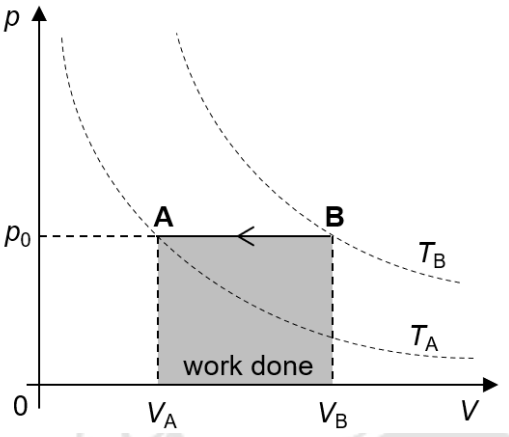
- Internal energy increases, ΔU is ***positive***

Process	Q	W	ΔU
A to B	+	–	+

By the 1st Law of Thermodynamics:

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

Isobaric Compression



In any compression, volume increases,

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

Temperature decreases from B to A

- Internal energy decreases, ΔU is ***negative***

Process	Q	W	ΔU
B to A	–	+	–

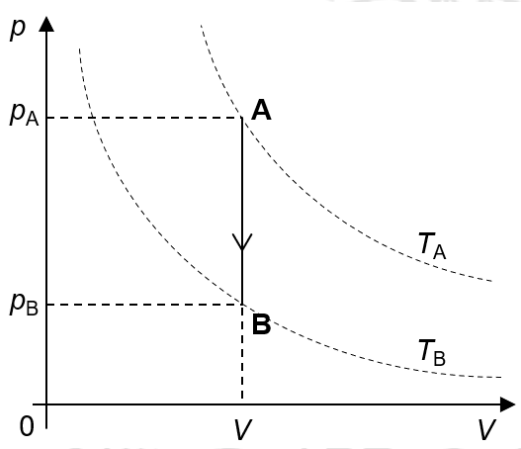
By the 1st Law of Thermodynamics:

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

(3) Constant Volume (Isovolumetric / Isochoric / Isometric)

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

Decrease in Pressure



There is no change in volume

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

Temperature decreases from A to B

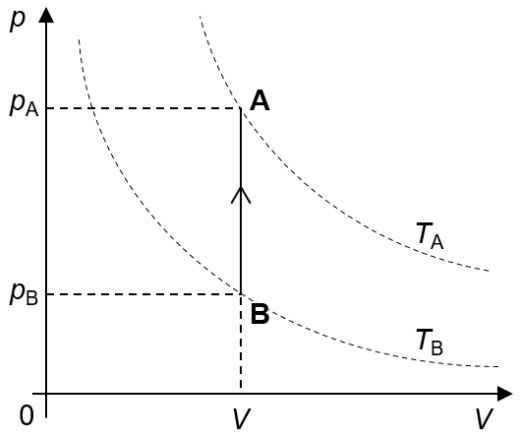
- Internal energy decreases, ΔU is *negative*

Process	Q	W	ΔU
A to B	–	0	–

By the 1st Law of Thermodynamics:

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

Increase in Pressure



There is no change in volume

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

Temperature increases from B to A

- Internal energy decreases, ΔU is *positive*

Process	Q	W	ΔU
B to A	+	0	+

By the 1st Law of Thermodynamics:

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

(4) No Heat Transfer (Adiabatic, $Q = 0$)

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

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

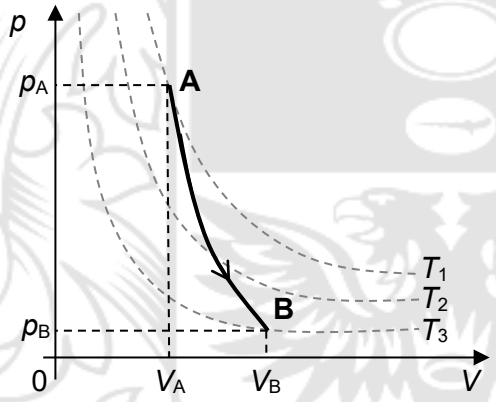
Such a process can be attained in the following cases:

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

Applying the ideal gas equation:

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

Adibatic Expansion



There is no heat transfer

- $Q = 0$

In any expansion, volume increases,

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

Temperature decreases from A to B

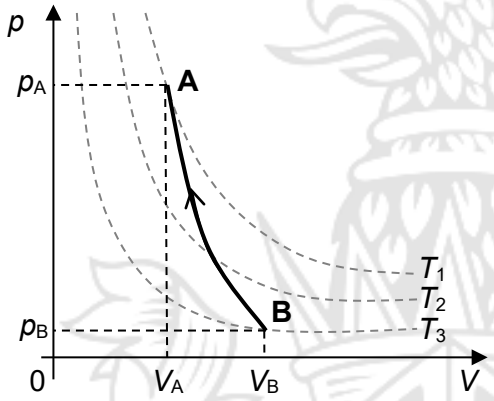
- Internal energy increases, ΔU is *negative*

Process	Q	W	ΔU
A to B	0	–	–

By the 1st Law of Thermodynamics:

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

Adibatic Compression



There is no heat transfer

- $Q = 0$

In any compression, volume increases,

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

Temperature increases from B to A

Internal energy increases, ΔU is ***positive***

Process	Q	W	ΔU
B to A	0	+	+

By the 1st Law of Thermodynamics:

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

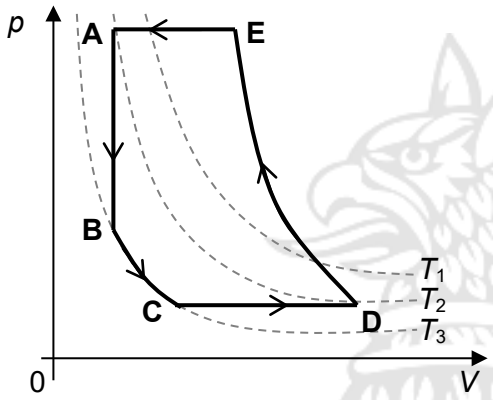
(5) Cyclic Process

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

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

The Diesel Cycle

Anti-clockwise



Internal Energy is state dependent

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

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

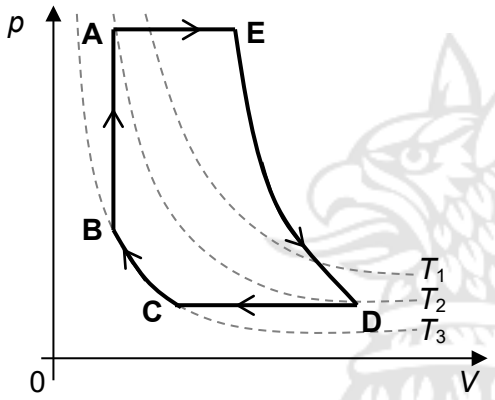
- More work is done during *compression (D to E to A)* than during *expansion (A to B to C to D)*
- Net work done **ON** the system; *W* is *positive*.

Process	Q	W	ΔU
A to A	–	+	0

By the 1st Law of Thermodynamics:

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

Clockwise



Internal Energy is state dependent

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

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

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

Process	Q	W	ΔU
A to A	+	–	0

By the 1st Law of Thermodynamics:

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

Example 13.2

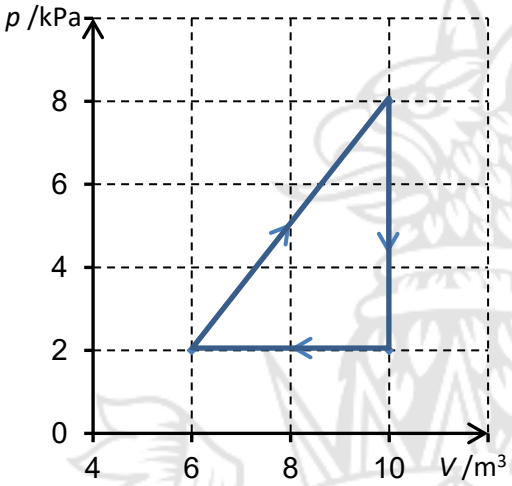
A system of gas with pressure p_1, volume V_1, and temperature T_1 undergoes process A by being heated at constant volume to pressure p_2, volume V_1, and temperature T_2. It then undergoes an expansion by process B at constant pressure to pressure p_2, volume V_3, and temperature T_3.

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

(a) Sketch the processes described on a *p*-*V* graph.
(b) State and explain which system has more internal energy at the end.

Example 13.3

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



(a) State whether net work done is on or by the gas and determine the net work done.

(b) State and explain the change in the internal energy of the gas during one complete cycle.

(c) Calculate the net heat transferred to the gas during one complete cycle.

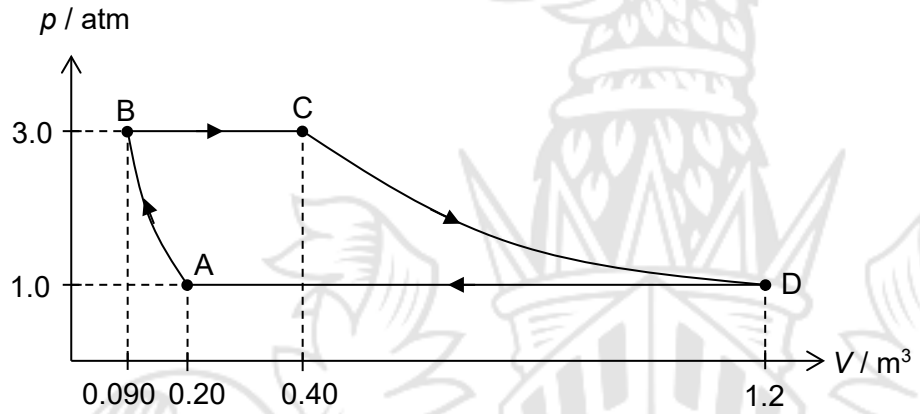
(d) Q is negative for the process BC and ΔU is negative for the process CA. Using the First Law of Thermodynamics, determine the signs of Q, W, and ΔU associated with each process. No calculations are required.

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

Example 13.4

A sample of an ideal gas goes through the processes shown in the figure below. From A to B, the process is adiabatic; from B to C, it is isobaric with 235.5 kJ of energy entering the system. From C to D, the process is isothermal and the work done by the gas is 133.5 kJ. From D to A, the process is isobaric with 253.3 kJ of energy leaving the system.

(1 atm pressure = 1.013×10^5 Pa)



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

Section of Cycle	Q	W	ΔU
A → B	0		
B → C	235.5 kJ		
C → D		–133.5 kJ	
D → A	–253.3 kJ		

13.4 Specific Heat Capacity and Specific Latent Heat

❖ Change of Phase

Heat capacity is related to changes in microscopic KE which involve changes in temperature, while latent heat is related to changes in microscopic PE which do not involve any changes in temperature, but the bonds between the particles change due to the absorption or release of heat. Fig. 13.4 shows the different possible processes that can occur between the different phases of a substance.

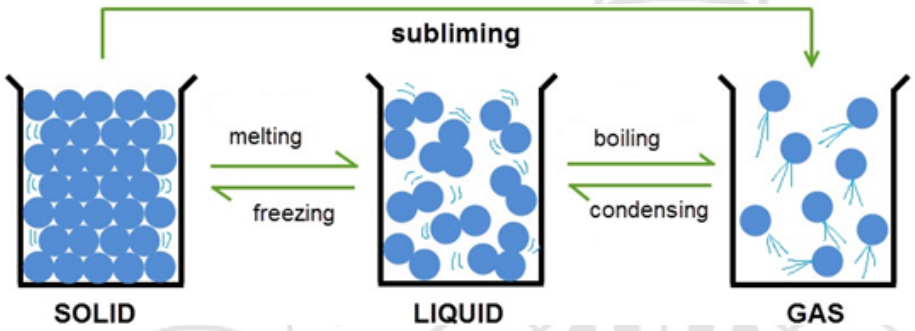


Fig. 13.4

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

Latent heat of fusion (solid → liquid)

Latent heat of vaporisation (liquid → gas)

The transition from one phase to another is not instantaneous. During transition, the two phases coexist until the transition is completed. Fig. 13.5 below shows the heating curve of a substance and its phase at various temperatures.

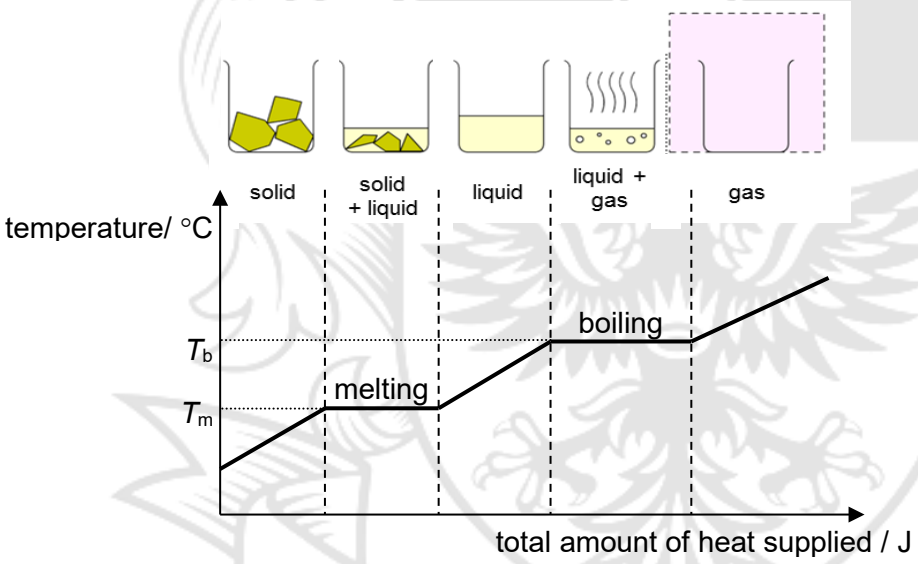


Fig. 13.5

What happens during a change of phase:

	Melting	Boiling
transition	• Solid to liquid	• Liquid to gas
inter-particle interactions	• Lattice structure has to break. Some bonds are broken.	• All bonds between particles have to be <u>completely</u> broken.
at melting point or boiling point	• particles have enough microscopic KE such that the amplitude of vibration is great enough to break some of the bonds between particles • the lattice structure collapses • change of phase occurs	• heat supplied is used to <u>completely</u> break the bonds between particles. • change of phase occurs
energy supplied	**Latent heat of fusion**	**Latent heat of vaporisation**
temperature	**During the processes of melting and boiling, the temperature remains constant.**	

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

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

What are the differences between boiling and evaporation?

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

Why does a cooling effect accompany evaporation?

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

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

Illustration of the cooling effect of evaporation

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

Total kinetic energy = **10 J**

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

New total kinetic energy = **8 J**

New average kinetic energy of the remaining molecules = **0.889 J**

The rate of evaporation can be increased by:

(i) increasing the area of the liquid surface

(ii) increasing the temperature of the liquid

(increasing average microscopic kinetic energy of all the molecules)

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

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

❖ Specific Heat Capacity

Heat Capacity

Heat Capacity at Constant Volume

Definition of Heat Capacity

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

Mathematically, this definition can be expressed as

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

where C = heat capacity

Q = quantity of heat

ΔT = change in temperature

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

Specific Heat Capacity

Definition of Specific Heat Capacity

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

Mathematically, this definition can be expressed as

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

where c = specific heat capacity

Q = quantity of heat

m = mass of body

ΔT = change in temperature

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

Determination of Specific Heat Capacity

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

Solids

For solids, the material under test is in the form of a solid cylinder of mass *m*, into which two holes are drilled to accommodate a heater and thermometer. The heater is powered by a low voltage dc supply and the variable resistor in the circuit allows potential difference and current through the heater to be varied. Fig. 13.6 shows the experimental set-up.

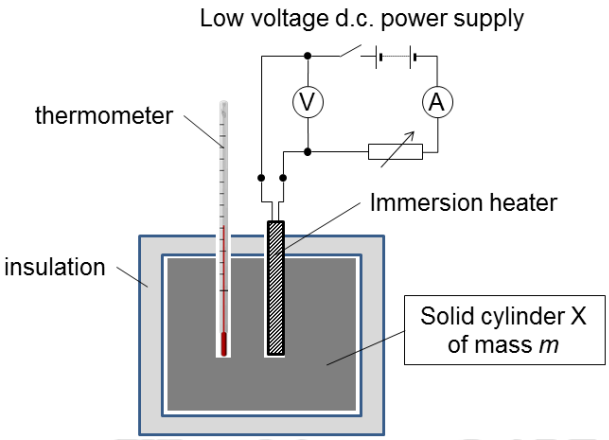


Fig. 13.6

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

Calculations

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

electrical energy supplied by heater = heat transferred to solid

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

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

Gases or Liquids

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

In this method, a steady flow of the fluid (liquid or gas), is passed along a pipe containing a heating coil. Measurements are only taken when the inlet and outlet temperatures have stabilised (i.e. the system has reached steady state). As such, the heat capacity of the apparatus can be ignored. Fig. 13.7 shows the experimental set-up.

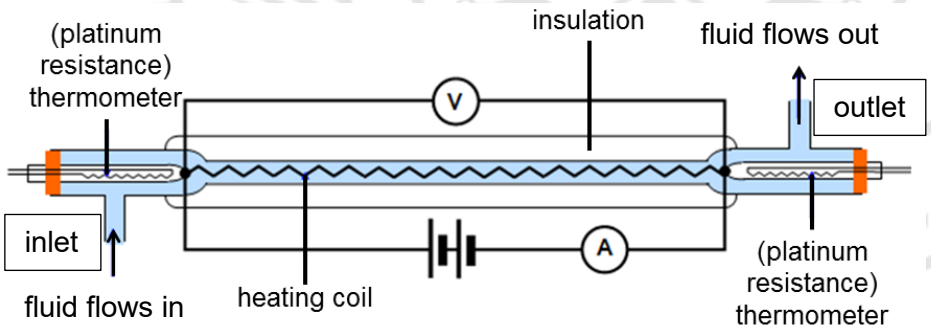


Fig. 13.7

Calculations

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

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

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

Rearranging the above,

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

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

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

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

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

Further Calculations

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

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

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

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

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

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

Example 13.5

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

(a) Calculate the heat gained by

(i) the water,

(ii) the kettle.

(b) Determine the fraction of the total energy used in heating the water.

Example 13.6

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

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

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

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

(b) the specific heat capacity of oil.

❖ Specific Latent Heat

Latent Heat

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

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

Definition of Specific Latent Heat of Fusion

The specific latent heat of fusion is the quantity of heat per unit mass required to convert a body from solid to liquid phase without any change of temperature.

Definition of Specific Latent Heat of Vaporisation

The specific latent heat of vaporisation is the quantity of heat per unit mass required to convert a body from liquid to gas phase without any change of temperature.

Mathematically, this definition can be expressed as

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

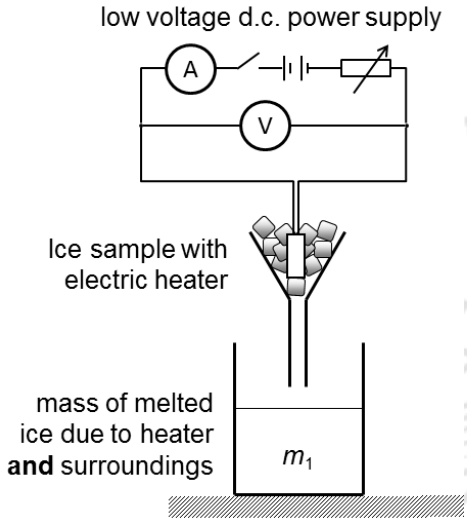
To determine Specific Latent Heat

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

To determine Specific Latent Heat of Fusion

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

The heater is then switched on and the current is kept constant. When water drips out of the funnel at a constant rate, the mass *M* melted in time duration *t* is determined. Fig. 13.8 shows the experimental set-up.



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

Fig. 13.8

Calculations

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

Electrical energy supplied	+	Heat from surroundings	=	Latent heat of fusion
$IV \times t$	+	ml_f	=	Ml_f
		IVt	=	$(M-m)l_f$
		l_f	=	$\frac{IVt}{M-m}$

Note:

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

To determine Specific Latent Heat of Vaporisation

An electric heater is immersed into a beaker of liquid that is placed on the pan of a balance. The heater is switched on and the current is kept constant. When the liquid boils at a steady rate, the change in the reading *m* on the balance in a time duration *t* is determined. Fig. 13.9 shows the experimental set-up.

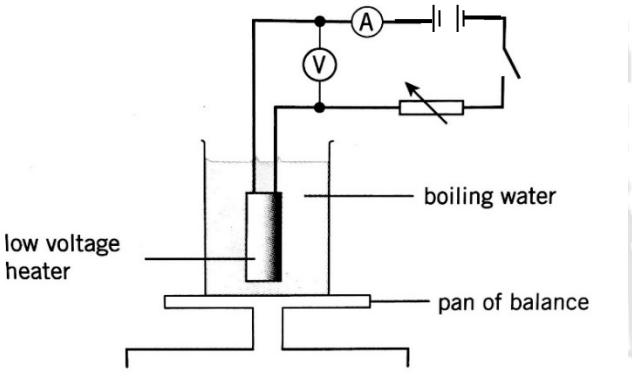


Fig. 13.9

Calculations

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

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

$$I\ V \times t = ml_v + H$$

Rearranging the above,

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

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

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

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

Further Calculations

For the repeated experiment,

$$I'V' = \frac{m'}{t'}l_v + \frac{H'}{t'} \qquad \text{..... (2)}$$

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

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

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

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

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

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

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

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

Example 13.7

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

(a) the time taken to heat the water to its boiling point

(b) the mass of water is boiled away in 5.0 min, starting from the time when the temperature of the water is 20 °C .

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

Example 13.8

Ice at 0 °C is added to 200 g of water initially at 70 °C in a vacuum flask. When 50 g of ice has been added and has all melted, the temperature of the flask and contents is 40 °C. When a further 80 g of ice is added and has all melted, the temperature of the flask and contents is 10 °C.

Calculate the specific latent heat of fusion of ice, neglecting any heat lost to the surroundings.

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

13.5 Appendix

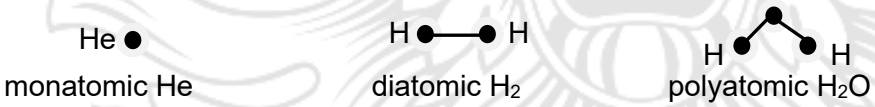
❖ Internal Energies of Monatomic, Diatomic And Polyatomic Gases

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

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

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

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



monatomic He | diatomic H_2 | polyatomic H_2O

❖ Phases of matter

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

NOTETAKING

"The 2nd law of thermodynamics has the same degree of truth as the statement that if you throw a tumblerful of water into the sea, you cannot get the same tumblerful of water out again."