

H2 Topic 9 – First Law of Thermodynamics



Aircon Compressors. Air-conditioned environments provide a welcome respite from the tropical humidity. "Blower" units in interiors have refrigerant connected to the compressor which usually sits outdoors. The compressor pressurizes the refrigerant and passes the heated liquid through fins cooled down by a fan. The refrigerant is further cooled by adiabatic expansion, and re-circulated back into the blower units, ready to transport more thermal energy from the interiors. As a cyclic process, there is net work done on the refrigerant i.e. there is more energy usage to operate the aircon system than the thermal energy the aircon system is able to extract.

Content

- Specific heat capacity and specific latent heat
- Internal energy
- First law of thermodynamics

Learning Outcomes

Candidates should be able to:

- (a) define and use the concepts of specific heat capacity and specific latent heat
- (b) show an understanding that internal energy is determined by the state of the system and that it can be expressed as the sum of a random distribution of kinetic and potential energies associated with the molecules of a system
- (c) relate a rise in temperature of a body to an increase in its internal energy
- (d) recall and use the first law of thermodynamics expressed in terms of the increase in internal energy, the heat supplied to the system and the work done on the system.

9.0 Introduction

For the first part of this topic, we return to the *macroscopic* scale to discuss how heat and temperature relates to work and energy. Devices which convert thermal energy into mechanical motion are typically referred to as *engines*.

We then bridge the above to the *microscopic* view and see how the interplay between energy and useful work is explained by the kinetic model of gases.



4-stroke internal-combustion petrol engine. The air-fuel mixture is compressed almost instantaneously – i.e. work is done on the gas. A spark ignites the air-fuel mix, resulting in great increases in pressure. The piston is pushed downwards and the gas does work by exerting the force (pressure applied on the piston surface) downwards and turning the crank shaft.



9.1 What does "specific" mean?

Similar to the idea of "GDP per capita" (normalizes economic output to *per* person basis), "population density" (normalizes number of people to *per* area basis) and "density" (normalizes mass to *per* unit volume basis), "*specific*" in thermal physics normalizes the quantity to a *per unit mass* basis.

A specific quantity in thermal physics allows us to discuss an intrinsic property of a material.

9.2 Raise Temperature within the Same Phase

Specific heat capacity is the thermal energy <u>per unit mass</u> to raise the temperature of a *substance* by one degree. $(\text{recall } Q = mc\Delta T)$ $C = \frac{Q}{m\Delta T}$ [S.I. unit: J kg⁻¹ K⁻¹] c = specific heat capacity

Q = quantity of thermal energy ΔT = change in temperature

a material, notice the definition involves substance rather than a *body*.

Since specific heat capacity discusses the property of

Experiments for finding specific heat capacity need to

- a find the mass,
- **b** measure the temperature rise,

c determine the quantity of thermal energy supplied (often by electrical means so
$$E = Pt = Q$$
)

d(i) prevent unwanted heat loss from the setup to surrounding OR

d(ii) permit the heat loss at a desired rate so as to accommodate calculations involving it.

Example 1

A 2.5 kg block of copper is wrapped in insulation. The block has 2 holes drilled to fit a thermometer and an electric heater. The heater has a constant effective resistance of 9.6 Ω and is connected to a benchtop constant-voltage supply. A rise of 50 °C is seen after 36.0 V is supplied for 6 minutes. Determine the specific heat capacity of the copper material.





eunoia

A 250 W heater is used to heat up 300 g of sea water contained in a calorimeter with a heat capacity of 230 J K⁻¹. The temperature of the sea water was initially 25.0 °C. After 130 s of heating, it reached a maximum of 45.0 °C. Find the specific heat capacity of sea water. State an assumption you made in your calculation.



Assumed all thermal energy from heater transferred to sea water and calorimeter without loss to surroundings.

Example 3

liquid out. Liquid enters a tube at a constant temperature 25.5 °C tube temperature of 19.5 °C. The mass of liquid flowing through the tube per unit time is m. ***** Electrical power P is dissipated in the heating liquid in. heating coil. A student found 2 sets of *m* and T temperature 19.5 °C coil P where liquid exits the tube at 25.5 °C. P/W $m/g s^{-1}$ (a) Suggest why the student obtains two sets of data rather than one. 33.3 1.11 (b) Find the specific heat capacity of the liquid. 1.58 44.9

(a) to account for heat loss from tube to surrounding [not allowed: stop/prevent heat loss]

(b) By Principle of Conservation of Energy, $\frac{energy from}{heater} = \frac{energy to raise}{temperature} + \frac{heat loss to}{surrounding}$

in 1 second, $P = mc\Delta T + h_{loss}$ $P_1 = m_1c\Delta T + h_{loss}$; $P_2 = m_2c\Delta T + h_{loss}$

$$P_{1} - P_{2} = (m_{1} - m_{2})c\Delta T$$

$$c = \frac{P_{1} - P_{2}}{(m_{1} - m_{2})\Delta T}$$

$$= \frac{44.9 - 33.3}{((1.58 - 1.11) \times 10^{-3})(25.5 - 19.5)}$$

$$= 4110 \text{ J kg}^{-1} \text{ K}^{-1}$$

Note: Recall that *temperature difference provides 2 pieces of info, (i) direction of heat flow (from heated water to surrounding) and (ii) rate of heat transfer (the larger the difference in temperature, the faster the rate).* This **continuous flow** method is suitable for gases and liquids. The **temperature at the inlet and outlet is the same across 2 data sets** (so temperature difference between inlet vs surrounding is same; temperature difference between outlet vs surrounding is another but same value) – so rate of heat loss to surrounding, h_{loss} , is same for both experiment runs.







9.3 Change Phase at Same Temperature

A pure substance will undergo phase change at one constant temperature, whereas mixtures will under phase change over a range of temperatures. phase change takes time – during the transition the phases coexist (across a phase boundary) until the phase change is completed.

> Specific latent heat is thermal energy per unit mass to change the phase of a substance* at constant temperature.



*To adapt the definition for specific latent heat of fusion, add the phrase "from solid phase to liquid phase" after "change the phase of a substance..." Similarly, for specific latent heat of vaporisation, add the phrase "from liquid phase to gas phase" after "change the phase of a substance..."

Experiments for finding specific latent heat capacity need to

- а find the mass,
- determine the quantity of thermal energy supplied (often by electrical means so E = Pt = Q) b
- c(i) prevent unwanted heat loss from the setup OR

c(ii) permit the heat loss at a desired rate so as to accommodate calculations involving it.

The requirements differ from that for finding specific heat capacity because there is no need to measure temperature change. However, a thermometer may still be needed to monitor

- (i) the substance is pure (same constant temperature during process), or
- (ii) the start and end of the phase change process.

Example 5

Water, in a beaker on a top pan balance, is maintained at boiling point using a heater. The change M in the balance reading after 300 s is given for 2 different power values to the heater. Find the specific latent heat of vaporization of water.

V / V	I/A	<i>M /</i> g
11.5	5.2	5.0
14.2	6.4	9.1

 $(P_1 - P_2)t = (m_1 - m_2)L_{v}$

 $= 2.27 \times 10^{6} \text{ J kg}^{-1}$





A heater is immersed in melting ice contained in a funnel. When the ice is melting at a constant rate, the mass m of ice melted in 5.0 minutes is noted, together with the power P of the heater. The power of the heater is then increased. A new reading for the mass m of ice melted in 5.0 minutes is recorded when the ice is melting at a constant rate.

0	
P/W	<i>m /</i> g
70	78
110	114

(a) Find the specific latent heat of fusion L of ice.

(b) Find rate of heat gained by ice from surroundings

Let *h*_{gain} be rate of heat gain from surroundings. By Principle of Conservation of Energy:

energy from heat from latent heat heater + surrounding of fusion $P_1t + h_{gain}t = m_1L_f$ $h_{\text{gain}} = \frac{m_1 L_{\text{f}}}{t} - P_1$ $P_1t + h_{\text{gain}}t = m_1L_f$; $P_2t + h_{\text{gain}}t = m_2L_f$ $(P_1 - P_2)t = (m_1 - m_2)L_f$ $=\frac{(114\times10^{-3})(3.33\times10^{5})}{5\times60}-110$ $L_{\rm f} = \frac{(P_1 - P_2)(t)}{(m_1 - m_2)} = \frac{(110 - 70)(5 \times 60)}{((114 - 78) \times 10^{-3})}$ = 16.5 W $= 3.33 \times 10^5 \text{ J kg}^{-1}$

Note: Constant temperature difference is maintained between ice point and room temperature so rate of heat gain from surroundings is same in both runs of experiment.

Example 7

A 35 W heater is immersed in ice melting at a constant rate. With the heater off, the mass m of ice melted in 2.0 minutes is 25 g. The heater is then switched on. When ice is melting at a new constant rate, m in 1.0 minute is 18.9 g. Find the specific latent heat of fusion *L* of ice.



By Principle of Conservation of Energy, latent heat to melt ice is from heater and environment. Let h_{gain} be rate of heat gain from surroundings:

energy from heat from latent heat heater + surrounding of fusion

 Pt_{heat}

$$P + h_{\text{gain}} t_{\text{heated}} = m_{\text{heated}} L_{\text{f}} \qquad ; h_{\text{gain}} t_{\text{hot heated}} = m_{\text{hot heated}} L_{\text{f}}$$
$$P + h_{\text{gain}} = \frac{m_{\text{heated}}}{t_{\text{heated}}} L_{\text{f}} \qquad ; h_{\text{gain}} = \frac{m_{\text{hot heated}}}{t_{\text{hot heated}}} L_{\text{f}}$$

$$L_{\rm f} = P \div \left(\frac{m_{\rm heated}}{t_{\rm heated}} - \frac{m_{\rm not heated}}{t_{\rm not heated}}\right) = 35 \div \left(\frac{18.9 \times 10^{-3}}{1.0 \times 60} - \frac{25 \times 10^{-3}}{2.0 \times 60}\right)$$

= 3.28 × 10⁵ J kg⁻¹

Note: Can regard the run w/o heater as "the control run".







Distinguish between melting, evaporation and boiling.

	melting	evaporation	boiling
phase change	solid to liquid	liquid to gas	liquid to gas
location	at phase boundary between solid and liquid	from liquid surface	throughout liquid
temperature	at specific temperature at melting point	at all temperatures	at specific temperature at boiling point

To increase the rate of evaporation:

- increase surface area of the liquid-gas phase boundary
- increase temperature of liquid: increases average kinetic energy of liquid particles so there is larger proportion of particles having enough kinetic energy to leave liquid phase
- induce draught ('wind') over liquid-gas phase boundary to remove gas particles before they have a chance of returning to the liquid phase
- reduce air pressure at the liquid-gas phase boundary to decrease chance of gas particle colliding with air molecules back to the liquid phase

Example 9

The specific heat capacity of ice and water is 2110 J kg⁻¹ K⁻¹ and 4200 J kg⁻¹ K⁻¹ respectively. A block of ice, of mass 900 g, is initially at - 5.0 °C. After being heated under constant atmospheric pressure at a constant 400 W for 15 minutes, the end state is 900 g of liquid water at 15.0 °C. (a) Suggest how to confirm that the block of ice is pure. (b) Determine the specific latent heat of fusion of water, assuming no heat loss to surrounding. (a) Use thermometer to measure temperature of the ice. Use stopwatch to measure the time elapsed from the start of heating. Track the variation of temperature with time. OR Use temperature sensor connected to a data-logger to measure the change in temperature of ice with respect to time elapsed from start of heating. [either way] if ice is pure, the melting takes place at a fixed constant melting point temperature. (b) By Principle of Conservation of Energy energy from energy to raise temperature of ice fusion temperature of water $Pt = mc_{ice}\Delta T_{ice} + mL + mc_{water}\Delta T_{water}$ $L = \frac{Pt}{m} - c_{\rm ice} \Delta T_{\rm ice} - c_{\rm water} \Delta T_{\rm water}$ $=\frac{(400)(15\times60)}{900\times10^{-3}}-(2110)(5)-(4200)(15)$ $= 326\ 000\ J\ kg^{-1}$



9.4 Internal Energy

Earlier we discussed specific heat capacity and specific latent heat – these are *processes* by which we *supply or extract* heat from a system. We need a way to describe the *state* of energy of particles (in the kinetic theory) before we can relate the *processes* to the system of particles.

Internal energy of a system is usually represented by U. It is a (mathematical) function of *states* – the internal energy of a system depends on states of the system such as p, V, T.

The concept of internal energy applies to substances in all phases – it is not exclusively used to discuss gases only.

Internal energy is the
sum of kinetic energies due to random motion of a distribution of particles
and potential energies due to intermolecular forces between the particles.

9.4.1 Internal Energy is not affected by Bulk Movement or Positioning

We distinguish between (i) the kinetic and potential energies *of the particles* in a system against (ii) the kinetic and potential energies of the system on a whole.

Consider the gas particles in a tank of compressed gas kept at constant temperature:

Scenario	Kinetic Energy (KE)	Potential Energy (PE)
Student carries tank and starts to run laps	Internal KE: no change	Internal PE: no change
around Level 7 corridor	Bulk KE: from zero to $\frac{1}{2}m_{gas}v_{student}^{2}$	Gravitational PE: no change
Student carries tank	Internal KE: no change	Internal PE: no change
Level 1 to Level 12	Bulk KE: no change (if initial and final speed of student is 0)	Gravitational PE: increased by $m_{gas}gh_{12 \text{ floors}}$



9.4.2 Microscopic Potential Energy

The larger the intermolecular separation, the larger the potential energy between particles.

Energy is needed to *break bonds* between particles during phase changes such as melting or boiling – we can deduce that intermolecular forces are attractive in nature.

Because of the small masses of particles, gravitational attraction between particles is insignificant. So intermolecular forces (e.g. *id-id* or *pd-pd* for Chemistry students) are largely due to electric forces.

9.4.3 Microscopic Kinetic Energy

Particles are in constant random motion (translation, rotation and vibration). In general, (thermodynamic) temperature is a measure of the average kinetic energy of particles in a system.

9.4.4 Internal Energy of an Ideal Gas

Ideal gas particles are assumed to be identical *spheres* that have no intermolecular forces in between. Hence there is only translational kinetic energy.

We revisit how temperature reflects kinetic energy of gas particles from previous topic:

In ideal gas, there is no intermolecular forces between particles. Hence, there is no potential energy, and internal energy is solely sum of kinetic energies of gas particles

$$U = \sum KE + \sum PE$$
$$U_{\text{ideal gas}} = \sum KE + 0$$

Mean *translational* kinetic energy of particles is directly proportional to thermodynamic temperature of gas.

$$U_{\text{ideal gas}} = N \langle E_{\text{K}} \rangle = \frac{3}{2} N k T = \frac{3}{2} n R T = \frac{3}{2} p V$$

In reality, molecules are not simple spheres. Because of geometry and chemical bonds, there exists other forms of kinetic energy such as rotational and vibrational KE.

Such considerations do not apply to gas particles in an ideal gas:

- No rotational consideration: a sphere looks the same no matter which axis you choose to rotate it on.
- No vibrational consideration: there are no chemical bonds between atoms to permit vibration.



Being able to move in x, y and z direction means 3 degrees of freedom (3DOF). Every DOF grants $\frac{1}{k}kT$ worth of internal energy therefore $U_{monoatomic} = 3/2$ NkT. Check out <u>Equipartition Theorem</u> for interested students.



9.5 First Law of Thermodynamics

The First Law of Thermodynamics is a statement of the Principle of Conservation of Energy.

First Law of Thermodynamics states that
$$\Delta U_{increase} = Q_{to} + W_{on}$$
the increase in internal energy of a system is the
sum of heat supplied to system and
work done on system
$$\Delta U : increase in internal energy (J)$$
 $\Delta U : increase in internal energy (J)$ $Q_{to} : heat given to system (J)$ $W_{on}: work done on system$

This equation discuss how the change in *state* of the system ΔU is effected by the *processes* of heat flow *Q* and the work done on the system *W*.

When we consider the *microscopic* perspective of Internal energy *U*, we can see how *macroscopic* processes of energy transfer (involving temperature differences and/or changes in phase) and mechanical work (involving forces and displacement) is explained by the kinetic theory of matter.

In more-**layman** speak: gas, which is enclosed in a container that can change volume and exchange energy, can act as an '*translator*' between *heat* and *forceful motion*. For cars, we *burn* fuel for heat to *drive* the wheels. For air-conditioning, we *compress* refrigerant to move heat.

9.6 Work Done on Gas

Work done on gas,

$$W_{on} = -p_{ext}\Delta V$$

 $= -p_{ext} (V_{final} - V_{initial})$

Work done is defined, by convention, via pressure that is constant and external to the system.

The work done <u>by</u> gas $W_{\text{by gas}} = -W_{\text{on gas}}$.

As mechanical work done is the product of the force and the displacement in the direction of the force:



$$W = F.s$$

= [F_{ext}](Δx)
= [$p_{ext}(A)$](Δx)
= $-p_{ext}\Delta V$

In general, when a gas is compressed (by an external agent), there is positive work done <u>on</u> gas.

process	comparison of V	sign of $\Delta V = V_{\text{final}} - V_{\text{initial}}$	work done <u>by</u> gas $W_{\rm by} = -W_{\rm on}$	work done <u>on</u> gas $W_{on} = -p_{ext}\Delta V$
compression	$V_{ m final} < V_{ m initial}$	- ve	- ve	+ ve
expansion	$V_{ m final} > V_{ m initial}$	+ ve	+ ve	- ve



9.7 Explaining Phenomena using First Law of Thermodynamics and Internal Energy

We should consider the macroscopic states (p, V, T) and the relation to the microscopic view of kinetic energies and potential energies when *processes* are performed on the system.

The following framework is a suggestion to help frame guide the description of *states*:

	Microscopic	Macroscopic	
KE	average KE of particles in a system \rightarrow	is directly proportional to	Τ
		thermodynamic temperature of system	
PE	PE between particles is determined by	for fixed mass and number of particles,	<i>V</i> ,
	intermolecular forces, which depends	the larger the volume, the greater the	phase
	on intermolecular separation \rightarrow	intermolecular separation.	
	ΔPE comes about because of	← Changes in volume can be small	
	changes in volume	when phase changes from solid to	
	and	liquid, and significant from liquid to	
		gas.	
	the breaking/formation of	A liquid/gas has no definite shape and	
	intermolecular bonds especially during	takes the shape of its container (since	
	phase changes.	particles can move about each other	
		rather freely).	

The First Law of Thermodynamics then allow us to discuss the processes where energy is supplied in the form of heat, or work done through the application of a force resulting in a change in volume.

Variation with time of temperature when heating pure water using constant-power heater





The following examples serve as practice for using this frame:

Example 10

During melting, a solid becomes liquid with little or no change in volume. Use kinetic theory to explain why thermal energy is required even though there is no change in temperature.

Thinking Process

	Microscopic	Macroscopic	
KE	1b) constant average KE of particles	← 1a) constant temperature so	Т
		4) By 1 st Law of Thermodynamics,	
		$\uparrow U$ is due to thermal energy supplied	
		$\left(\Delta U = Q_{\text{to}} + W_{\text{on}}\right)$	
		$\left(= (+ ve) + 0 \right)$	
PE	3a) rigid intermolecular bonds in solid	2a) negligible volume change	Vor
	lattice broken	$(\Delta V \approx 0)$	phase
	3b) PE between particles \uparrow $\begin{pmatrix} U = \sum KE + \sum PE \\ \Delta U = 0 + (\uparrow PE) \end{pmatrix}$	2b) negligible w.d. on system $(W_{on} \approx 0)$	

Solution

[Aim: use $\Delta U = Q_{to} + W_{on}$ and kinetic theory to show that $Q_{to} > 0$]

[U = KE + PE]

There is no change in temperature, so the average KE of particles is constant.

i.e. ΔKE is zero.

<u>Rigid intermolecular bonds in solid lattice are broken</u>, so <u>potential energy</u> between particles is <u>increased</u>. Hence <u>internal energy of substance increases</u>.

i.e. ΔU is positive

[*W*]

There is <u>negligible change in volume</u>, so there is <u>negligible work done on system</u>. i.e. W_{on} is zero.

 $[\Delta U = Q_{\rm to} + W_{\rm on}]$

By First Law of Thermodynamics, internal energy increases while no work is done <u>on</u> system, so there must be thermal energy provided to the system. i.e. *Q*_{to} is positive



Energy has to be supplied continuously during boiling of water. Explain how internal energy is increased.

Thinking Process

	Microscopic	Macroscopic	
KE	1b) constant average	← 1a) constant temperature so	Τ
	KE of particles		
		4) Supply of thermal energy is to completely break	
		intermolecular bonds and for system to do work	
		against atmosphere	
PE	3a) intermolecular	2a) large increase in volume for phase change from	Vor
	bonds completely	liquid to gas	phase
	broken		
		2b) w.d. <u>by</u> system	
	3b) PE between	against atmosphere	
	particles ↑		
	$(U = \sum KE + \sum PE)$	$(W_{by} = -W_{on})$ ext	ernal
		$= p_{out} \Delta V$ (enclosed as) pre	ssure
	$\left(\Delta U = 0 + (PE)\right)$	$\left - n \left(V - V \right) \right $	P _{ext}
			*
		(= (+ ve))	

Note: The choice of argument has to be deliberate to cater to question. If the argument goes via points 1, 2, and then by 1st Law of Thermodynamics, $\Delta U = Q_{to} + W_{on} = (+ ve) + (- ve)$, the argument doesn't work as well.

Solution

[Aim: use $\Delta U = Q_{to} + W_{on}$ and kinetic theory to show that $\Delta U > 0$]

[*W*]

There is <u>a large increase in volume as water changes from liquid to gaseous phase</u>, so there is <u>work done by system</u>.

i.e. Won is negative.

[U = KE + PE]

There is <u>no change in temperature</u>, so <u>average KE of particles is constant</u>. Intermolecular bonds are broken during the change in phase from liquid to gas, so potential <u>energy is increased</u>. Hence <u>internal energy of substance increases</u>. i.e ΔU is positive

 $[\Delta U = Q_{\rm to} + W_{\rm on}]$

By First Law of Thermodynamics, internal energy increases while work is done by the system, so there must be thermal energy provided to the system, such that $Q_{to} > |W_{on}|$.



Explain why, in general, the specific latent heat of vaporisation of a substance is larger than the specific latent heat of fusion.

Thinking Process

	Microscopic	Macroscopic	
KE	1b) no change in average KE of particles in	← 1a) constant temperature so	Τ
	both processes		
PE	3) intermolecular bonds completely broken	2a) much larger increase in	Vor
	for phase change from liquid to gas.	volume for phase change from	phase
		liquid to gas as compared to	
	bonds are partially broken when breaking	solid to liquid	
	rigid solid lattice to become liquid.		
		2b) more w.d. against	
	3b) more energy needed to ↑PE between	atmosphere during liquid-gas	
	particles during liquid-gas phase change	phase change	

Solution

[Aim: use $\Delta U = Q_{to} + W_{on}$ and kinetic theory, to show that latent heat (related to Q_{to}) for vaporisation is larger than that for fusion]

[*W*]

There is a <u>larger increase in volume</u> when substances change phase from liquid to gas as compared to when they change phase from solid to liquid, so more work is done by system on the atmosphere.

i.e. W_{on} is more negative for change in phase from liquid to gas, than solid to liquid.

[U = KE + PE]

There is <u>no change in temperature in both processes</u>, so average KE of particles is constant in both processes.

Intermolecular bonds are completely broken during phase change from liquid to gas but only partially broken during the phase change from solid to liquid, so the increase in potential energy between particles is greater for vaporisation. Hence internal energy of substance increases more for vaporisation.

i.e ΔU is more positive.

 $[\Delta U = Q_{\rm to} + W_{\rm on}]$

There is more work done by the system on the atmosphere and greater increase in internal energy for vaporisation, so by First Law of Thermodynamics, <u>more thermal energy</u> must be provided to the system. Hence, specific latent heat of vaporisation of a substance is larger than the specific latent heat of fusion.



Explain how evaporation brings about cooling of the liquid left behind.

Thinking process

	Microscopic	Macroscopic	
KE	1) liquid particles in constant random motion		Т
	2) wide range of speed in the distribution of particles so there are always some particles with high speeds		
	4a) $\downarrow \langle E_{k} \rangle \rightarrow$	4b) ↓ <i>T</i>	
PE	3) if high speed particles are near surface they can escape the attractive intermolecular forces and move into gas phase		V or phase

Solution

The particles in a liquid are in constant random motion and have a wide range of kinetic energies.

If the particles with high speed are near the liquid surface, they can escape from the surface to become vapour.

Since it is always the high speed particles that escape, the average kinetic energy of the remaining particles would be lower than before.

Hence the temperature of the liquid would fall and the liquid cools.

In a random distribution of liquid particles, the Maxwell-Boltzmann Distribution shows there is a small proportion of particles with high speeds.

If the particles that have more than sufficient kinetic energy to escape the intermolecular forces of the liquid phase (shaded) are near the liquid-gas phase boundary, they may escape, leaving behind the population that will have less total energy.





Example 14 (a)

By reference to work done and heating, explain why temperature of gas in balloon decreases when balloon bursts suddenly.

Thinking process

(a)	Microscopic	Macroscopic	
KE		3) By 1 st Law of Thermodynamics, internal energy \downarrow	Τ
	4a) average KE of gas particles ↓ →	$\begin{pmatrix} \Delta U = Q_{to} + W_{on} \\ = 0 + (-ve) \end{pmatrix}$ 4b) average KE is directly proportional to thermodynamic temperature, temperature \downarrow $\left(\langle E_{\kappa} \rangle = \frac{3}{2} kT \right)$	
PE	Note:	1) sudden ↑volume so insufficient time for heat to enter or leave	<i>V</i> ,
	expansion	gas $(Q=0)$	phase
	implies		
	but effect is	2) w.d. <u>by</u> gas against atmosphere as gas expands	
	less	$(W_{op} = -W_{by})$	
	significant to		
	↓KE		

Solution

[Aim: use $\Delta U = Q_{to} + W_{on}$ and kinetic theory to show that average KE drops]

 $[\Delta U = Q_{\rm to} + W_{\rm on}]$

The volume of gas expands suddenly in an adiabatic process so there is insufficient time for heat to enter or leave the gas.

i.e. Q_{to} is zero

There is work done by gas on the atmosphere.

i.e. *W*on is negative

By First Law of Thermodynamics, the internal energy of the gas has to decrease. i.e ΔU is negative

[U = KE + PE]

Internal energy is the sum of sum of kinetic energies due to random motion of a distribution of particles and potential energies due to intermolecular forces between the particles.

PE increases with larger intermolecular separation, so KE must have decreased more significantly, such that internal energy *U* decreases overall.

Since average KE of the gas particles is directly proportional to the thermodynamic temperature of the gas, as average KE decreases, temperature decreases.



Example 14 (b)

By reference to work done and heating, explain why internal energy of ice* increases when ice melts at constant temperature and at atmospheric pressure to form water that is more dense than the ice.

Thinking process

(b)	Microscopic	Macroscopic	
KE		3) By 1 st Law of Thermodynamics, internal energy \uparrow $\begin{pmatrix} \Delta U = Q_{to} + W_{on} \\ = (+ ve) + (+ ve) \end{pmatrix}$	Τ
PE		1) external w.d. <u>on</u> water as volume \downarrow $\begin{pmatrix} W_{on} = -p_{ext}\Delta V \\ = -p_{ext}(V_{final} - V_{initial}) \\ = (+ ve) \end{pmatrix}$	V, phase
	2b) supply thermal energy (Q_{to}) to break rigid intermolecular bonds in solid lattice	← 2a) solid phase to liquid phase	

Solution

[Aim: use $\Delta U = Q_{to} + W_{on}$ and kinetic theory to show that ΔU increases]

 $[\Delta U = Q_{\rm to} + W_{\rm on}]$

The volume of water decreases initially during melting so there is work done on the system of water.

i.e. *W*on is positive

Thermal energy is supplied to break rigid intermolecular bonds during phase change from solid to liquid, so there is increase in potential energy between particles. i.e. *Q*_{to} is positive

By First Law of Thermodynamics, the internal energy of the gas has to increase. i.e ΔU is positive

Note*: Need to be extra careful when working with water because it is unique. Most substances increase volume when melting and heating throughout liquid phase. But water is most dense (least volume) at 4 °C so need to take care when discussing work done or volume changes near melting point.

During melting, internal energy increases. We argue that KE remains constant at constant temperature *but PE increases due to the breaking of intermolecular bonds.*





9.8 Graphical Representation of States and Paths

Recall that the *state* of an ideal gas is described by its *p*, *V* and *T*. We can represent all states of an ideal on a 3D surface. By keeping one variable constant, we can generate 2D graphs to help us represent *states* and *processes*.



9.8.1 *p*-V Diagrams

Referring to 9.6, for expansion process:

p-*V* diagrams are a common graphical representation of changes in a *closed system* (no exchange of matter, but exchange of energy permitted). In particular, the area under the curve is related to the *work done* in that process.

- work done <u>by</u> gas $W_{\rm by}$ is positive - work done on gas Won is negative р final state p_{final} Magnitude of work done in the process proces is area under the *p*-*V* graph: p_{initial} initial state V V_{initial} V_{final} area under p-V graph gives magnitude of w.d.



For a fixed mass of ideal gas moving from state A to B:

- 1. increase in pressure $\Delta p = p_{\text{final}} p_{\text{initial}} = p_{\text{B}} p_{\text{A}}$
- 2. increase in volume $\Delta V = V_{\text{final}} V_{\text{initial}} = V_{\text{B}} V_{\text{A}}$
- 3. implies temperature increase

$$T = \frac{pV}{nR}$$
$$\Delta T = \frac{p_{\rm B}V_{\rm B} - p_{\rm A}V_{\rm A}}{nR}$$



- 4. implies increase in internal energy $\Delta U = \frac{3}{2} nR(\Delta T)$
- 5. By 1st Law of Thermodynamics, $\Delta U_{increase} = Q_{to} + W_{on}$. The same change in internal energy ΔU can be via different combinations of heat supply and work done, herein

$$|W_{(ii)}| > |W_{(i)}|$$

We say that work done *W* is *path dependent*. Heat transfer *Q* is also *path dependent*.

Change in *state functions* (e.g. ΔU) depends only on final and initial *states* and is independent of the path taken.

Internal energy *U* is a *state* function dependent on *state variables p*, *V*, *T*.

9.8.2 Isobaric Process

Isobaric process is one where the enclosed gas remains at <u>constant pressure</u>. $\Delta p = 0$ allows the (magnitude of) <u>work done to be conveniently found</u>:





9.8.3 Isovolumetric Process

Isovolumetric / Isochoric / Isometric processes is one where the enclosed gas remains at <u>constant</u> volume. $\Delta V = 0$ so no work done is done.

$$W_{\rm on} = -p\Delta V$$

= 0

By 1st Law of Thermodynamics , $\Delta U_{\text{increase}} = Q_{\text{to}} + W_{\text{on}}$ $\Delta U_{\text{increase}} = Q_{\text{to}} + 0$

All the heat supplied to the system results in an increase in its internal energy by the same amount.

If pressure decreases, temperature decreases. Since internal energy is directly proportional to temperature, internal energy decreases as heat is transferred away from system $Q_{to} < 0$.

If pressure increases, temperature increase. Since internal energy is directly proportional to temperature, internal energy increases as heat is transferred to system $Q_{to} > 0$.

9.8.4 Isothermal Process

Isothermal processes takes place at <u>constant temperature</u>. $\Delta T = 0$. For an <u>ideal gas, there is no</u> <u>change in internal energy</u>. For other substances, the <u>mean translational kinetic energy of particles</u> <u>remains constant</u>.



For all isothermal processes, a plot of *p* against $\frac{1}{V}$ will yield a straight line passing through origin and of gradient (*nRT*).







For an ideal gas,

$$pV = nRT$$
$$p_1V_1 = p_2V_2$$

Internal energy of ideal gas is directly proportional to its thermodynamic temperature:

$$\Delta U = \left(\frac{3}{2}nR\right)\Delta T$$

so $\Delta U = 0$

By 1st Law of Thermodynamics

$$\Delta U_{\text{increase}} = Q_{\text{to}} + W_{\text{on}}$$
$$0 = Q_{\text{to}} + W_{\text{on}}$$
$$Q_{\text{to}} = -W_{\text{on}}$$
$$= W_{\text{by}}$$



Earlier in the discussions for isobaric and isovolumetric processes, we noted that the temperature of the gas can change.

You can visualize that the final and initial states rest on different isotherms.





9.8.5 Adiabatic Process

Adiabatic processes takes place with <u>no heat supplied to or lost from the system</u>. Q = 0.

By 1st Law of Thermodynamics:

$$\Delta U_{\text{increase}} = Q_{\text{to}} + W_{\text{on}}$$
$$Q_{\text{to}} = 0$$
$$\Delta U_{\text{increase}} = W_{\text{on}}$$

To have an adiabatic process, either

- "sudden" process such that there is not enough time for heat exchange to take place between system and surrounding, or
- thermally insulated system from surrounding

Since there is no heat exchange, the temperature of the system will change across the process. Therefore, on a *p*-V diagram, adiabatic processes are steeper than isotherms.





9.8.6 Cyclic Process

In a cyclic process, the system starts and ends at the same state (same p, V, T). $\Delta U_{1 \text{ cycle}} = 0$.

Recall that the change in internal energy ΔU is a state function which only depends on the initial and final state (and is independent on the path taken).

By 1st Law of Thermodynamics,

$$\Delta U_{\text{increase}} = Q_{\text{to}} + W_{\text{on}}$$
$$0 = Q_{\text{to}} + W_{\text{on}}$$
$$Q_{\text{to}} = -W_{\text{on}}$$
$$= W_{\text{bv}}$$

Within a cycle, we discuss the idea of *net* work done for a given quantity of heat exchanged.





A fixed mass of ideal gas undergoes a cycle of changes of pressure, volume and temperature. Complete the table following.



	heat supplied / J	work done on gas / J	$\Delta U/J$
$A \rightarrow B$	0	(i) + 1200	+ 1200
$B \rightarrow C$	(vii) - 1350	(iii) <mark>0</mark>	- 1350
$C \rightarrow D$	0	(ii) - 600	- 600
$D \rightarrow A$	(iix) + 750	(iv) 0	(vi) + 750
sum of 4 processes	(ix) - 600	(x) + 600	(v) 0

Step 1) We can solve for (i) and (ii) first because of 1st Law:

By 1st Law of Thermodynamics:

$$\begin{split} \Delta U_{\text{increase}} &= Q_{\text{to}} + W_{\text{on}} \\ W_{\text{A} \rightarrow \text{B}} &= \Delta U_{\text{increase}} - Q_{\text{to}} \\ &= +1200 - (0) \\ &= +1200 \text{ J} \\ W_{\text{C} \rightarrow \text{D}} &= \Delta U_{\text{increase}} - Q_{\text{to}} \\ &= -600 - (0) \end{split}$$

$$= -600 - (0)$$

Step 2) Take note that (iii) and (iv) are isovolumetric processes so work done is zero.

Step 3) For (v), since change in internal energy ΔU is a state function which only depends on the initial and final state, $\Delta U_{1 \text{ cycle}} = 0$.

Step 4) (vi) can be found using $\Delta U_{1 \text{ cycle}} = 0$: $\Delta U_{1 \text{ cycle}} = +1200 - 1350 - 600 + \Delta U_{D \to A}$ $\Delta U_{D \to A} = 0 - (+1200 - 1350 - 600)$ = +750 J

Step 5) Apply 1st Law to (vii) and (iix)

 $\Delta U_{\rm increase} = Q_{\rm to} + W_{\rm on}$

By 1st Law of Thermodynamics:

 $Q_{B \to C} = \Delta U_{B \to C} - W_{B \to C}$ = -1350 - 0= -1350 J

$$Q_{D \to A} = \Delta U_{D \to A} - W_{D \to A}$$
$$= +750 - 0$$
$$= +750 \text{ J}$$

Note: There is net work done on gas; the energy was lost as heat leaving the gas. This is consistent: the cycle runs anti-clockwise on the *p*-*V* diagram. Extra: check that the states obey pV = nRT.



A fixed mass of ideal gas undergoes a cycle of changes of pressure, volume and temperature. Complete the table following.



	process	Q / kJ	W/kJ	$\Delta U/ kJ$
$A \rightarrow B$	adiabatic	0	+ 43	+ 43
$B \rightarrow C$	isobaric	+ 100	- 93	+ 7.0
$C \rightarrow D$	isothermal	+ 133.5	- 133.5	0
$D \rightarrow A$	isobaric	- 150	+ 100	- 50

Step 1) $C \rightarrow D$

Isothermal so $\Delta U_{C \rightarrow D} = 0$. By 1st Law, $\Delta U_{C \rightarrow D} = Q_{C \rightarrow D} + W_{C \rightarrow D}$ $Q_{C \rightarrow D} = \Delta U_{C \rightarrow D} - W_{C \rightarrow D}$ = 0 - (-133.5)= +133.5 kJ

Step 2) B \rightarrow C Isobaric so can find w.d. conveniently: $W_{B\to C} = -p\Delta V = -p(V_{final} - V_{initial})$ $= -(3 \times 10^5)(0.40 - 0.090)$ = -93 kJ

By 1st Law,

$$\Delta U_{\rm B\to C} = Q_{\rm B\to C} + W_{\rm B\to C}$$
$$= +100 + (-93)$$
$$= +7.0 \text{ kJ}$$

Step 3) $D \rightarrow A$

Isobaric so can find w.d. conveniently:

$$W_{D \to A} = -p\Delta V = -p(V_{\text{final}} - V_{\text{initial}})$$
$$= -(1 \times 10^5)(0.20 - 1.2)$$
$$= +100 \text{ kJ}$$

$$\Delta U_{D \to A} = Q_{D \to A} + W_{D \to A}$$
$$= -150 + (+100)$$
$$= -50 \text{ kJ}$$

Step 4) ΔU is cyclic, $\Delta U_{1 \text{ cycle}} = 0$ $\Delta U_{1 \text{ cycle}} = +7.0 + 0 + (-50) + \Delta U_{A \rightarrow B}$ $\Delta U_{A \rightarrow B} = 0 - (7.0 + 0 + (-50))$ = +43 kJ

Step 5) A
$$\rightarrow$$
 B by 1st Law

$$\Delta U_{A \rightarrow B} = Q_{A \rightarrow B} + W_{A \rightarrow B}$$

$$W_{A \rightarrow B} = \Delta U_{A \rightarrow B} - Q_{A \rightarrow B}$$

$$= +43 - 0$$

$$= +43 \text{ kJ}$$

Note: Typically the tables do not include "sum of all processes" as the last row. You should do it as a last check; in this case the cycle runs clockwise so there should be net work done by gas. Some tutors find solving such questions akin to solving Sudoku puzzles; have fun!



9.9 Summary

Action	To Consider	To Calculate
Change temperature of a substance within same phase	specific heat capacity is thermal energy <u>per unit mass</u> to raise the temperature of a <i>substance</i> by one degree kelvin	$c = \frac{Q}{m\Delta T}$
Change Phase at Same Temperature	specific latent heat is thermal energy <u>per unit mass</u> to change the phase of a substance* at constant temperature	$L = \frac{Q}{m}$

When performing experiments to find specific heat capacity or specific latent heat, you can either - prevent unwanted heat loss from the setup **OR**

- permit the heat loss at a desired rate so as to accommodate calculations accounting for it

Internal energy is the sum of kinetic energy due to random motion of a distribution of particles and potential energies due to intermolecular forces between the particles.

In an ideal gas, there are no intermolecular forces between particles so no potential energy, so the internal energy is solely sum of kinetic energy of gas particles.

$$U = \sum KE + \sum PE$$

 $U_{ideal gas} = \sum KE + 0$

The mean *translational* kinetic energy of particles is directly proportional to thermodynamic temperature of the ideal gas.

$$U_{\text{ideal gas}} = N \langle E_{\text{K}} \rangle$$
$$= \frac{3}{2} N k T = \frac{3}{2} n R T$$
$$= \frac{3}{2} p V$$

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

$$\Delta \textit{U}_{\text{increase}} = \textit{Q}_{\text{to}} + \textit{W}_{\text{on}}$$

The work done on gas is: $\frac{W_{on} = -p_{ext}\Delta V}{= -p_{ext} (V_{final} - V_{initial})}$

When explaining phenomena, consider the following framework:

	Microscopic	Macroscopic	
KE			Τ
PE			<i>V</i> ,
			phase



p-*V* diagrams are a common graphical representation of changes in a closed system; the area under the curve gives the magnitude of work done in that process.

Change in state functions (e.g. ΔU) depends only on final and initial states and is independent of the path taken.

Processes:

- Isobaric: constant pressure so magnitude of w.d. conveniently found.
- Isovolumetric: constant volume so no work done.
- Isothermal: constant temperature so mean translational KE of particles remain constant.
- Adiabatic: no heat supplied to or loss by system either through thermal insulation or through sudden process such that there is insufficient time for heat exchange to take place with surrounding.
- Cyclic: system starts and ends at the same state (same p, V, T). $\Delta U_{1 \text{ cycle}} = 0$

When net work is done \underline{By} gas, *p*-*V* cycle runs clockwise When net work is done \underline{On} gas, *p*-*V* cycle runs anti-clockwise.