

Topic 9 - First Law of Thermodynamics

1 Specific heat capacity and specific latent heat

1.1 Heat capacity

The numerical value of the heat capacity of a body is the quantity of heat required to raise the temperature of the body by one degree

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

1.2 Specific heat capacity

the numerical value of the specific heat capacity of a substance is the quantity of heat required to raise the temperature of the unit mass of the substance by one degree

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

1.3 Determination of specific heat capacity

For solids, since

$$IVt = mc(T_f - T_i)$$

$$c = \frac{IVt}{m(T_f - T_i)}$$

For gases or liquids, to account for heat loss

electrical energy supplied = heat transferred to liquid + HEAT LOSS to surrounding

$$IV \times t = mc(T_{out} - T_{in}) + H$$

$$IV = \frac{m}{t}c(T_{out} - T_{in}) + \frac{H}{t}$$

rate of heat loss $\frac{H}{t}$ is proportional to the excess temperature of the apparatus.

using a different set of I, V and flow rate,

$$I'V' = \frac{m'}{t'}c(T_{out} - T_{in}) + \frac{H'}{t'}$$

using the two sets of equations,

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

1.4 Kinetic model of matter

	solid	liquid	gas
packing arrangement of atoms/molecules	closely packed in lattice structure	slightly further apart than solids	very far apart
movement of atoms	vibrations about mean position	random motion throughout liquid	random motion at high speeds
intermolecular forces	strong intermolecular attractive and repulsive forces	attractive forces	negligible intermolecular forces

1.5 Change of phase

	Melting	Boiling
intermolecular interactions	lattice structure starts to break <ul style="list-style-type: none"> • molecules have enough energy to vibrate so violently that they are no longer held by attractive forces • the lattice structure collapses • change of state occurs 	all bonds between atoms/molecules completely broken <ul style="list-style-type: none"> • thermal energy supplied is used to overcome the attractive forces between molecules • bonds are completely broken • change of state occurs
energy supplied	latent heat of fusion	latent head of vaporisation

standard qualitative questions

- Why do melting and boiling take place without a change in temperature?
 - at melting: lattice structure collapses due to vibration of molecules and solid uner goes phase change
 - latent heat of fusion will not cause a change in temperature, and is used to overcome the attractive forces between atoms and causes the lattice structure to break
 - during boiling: intermolecular forces are completely broken
 - latent heat of evaporation used to overcome attractive forces between molecules
- Why is specific latent heat of vaporisation higher than the specific latent heat of fusion for the same substance?
 - To melt a solid, some molecular bonds are broken
 - to vaporise a liquid, all remaining bonds must be broken
 - more bonds broken during vaporisation
 - furthermore, work is needed to do work against the external or atmospheric pressure for gas to expand, since gas occupies a much larger volume than liquid
- Why is evaporation accompanied by cooling?
 - Kinetic theory supposes that molecules of liquids are at continual random motion and make frequent collisions with each other. During collision, some lose energy and some gain energy
 - if a molecule near the surface gains enough evergy, it will be able to escape from the attractive forces from the molecules below it
 - this results in a decrease in the average KE of the remaining molecule
 - since temperature is a measure of average KE, the liquid becomes colder

1.6 Latent heat

The numerical value of the specific latent heat of fusion is the quantity of heat required to convert unit mass of solid to liquid without any change in temperature

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

The numerical value of specific latent heat of fusion is the quantity of ehat required to convert unit masss of liquid to gas without any change in temperature

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

1.7 Determination of latent heat

For latent heat of fusion, to account for melting due to heat gained from surrounding

heat from electrical heater + heat gained from surrounding = latent heat of fusion

Let M be the total mass of ice melted and m be the mass of ice melted due to surroundings

$$IVt + ml_f = Ml_f$$

$$IVt = (M - m)l_f$$

$$l_f = \frac{IVt}{M - m}$$

For latent heat of vaporisation, to account for heat loss to the surrounding

$$IV = \frac{m}{t}l_v + \frac{H}{t}$$

$$I'V' = \frac{m'}{t'}l_v + \frac{H'}{t'}$$

$$l_v = \frac{IV - I'V'}{\frac{m}{t} - \frac{m'}{t'}}$$

2 Internal energy

The internal energy of a system is determined by the state of the system and it is the sum of the random distribution of kinetic and potential energies associated with the molecules of the system
The internal energy of a system is the sum of KE due to **random motion** of the molecules, and PE associated with the **intermolecular forces of the system**

Microscopic KE

$$\langle E_k \rangle = \frac{3}{2}kT$$

Microscopic PE

Molecules have PE due to intermolecular attraction and repulsion. Solids have the most negative PE

Effect of temperature A rise in temperature implies an increase in average KE, hence an increase in internal energy

2.1 Internal energy of an ideal gas

Since it is assumed that an ideal gas has **no intermolecular forces**, the internal energy of a gas is purely due to translational KE

for one molecule

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

For N molecules

$$\text{total } E_k = \frac{1}{2}Nm\langle c^2 \rangle = \frac{3}{2}NkT$$

Since the internal energy U of an ideal gas is purely kinetic

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

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

The **state** of a system is purely determined by p , V and T

- ΔU is solely dependent on T
- only a change in p or V which results in a change in T will cause a change in state

3 First law of thermodynamics

the **First law of thermodynamics** states that the increase in internal energy of a system is equal to the sum of 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

$$\Delta U = Q + W$$

	Positive (+)	Negative (-)
ΔU	increase in internal energy	decrease in internal energy
Q	Heat absorbed by the system	Heat loss by the system
W	Work done on system (compression)	Work done by system (expansion)

3.1 Work done, W

for a gas in an enclosed system with a frictionless, movable piston of area A , when gas expands, a force F is applied on the piston **by** the gas against external pressure p

work done on the gas is thus

$$W = - \int_{V_i}^{V_f} p dV$$

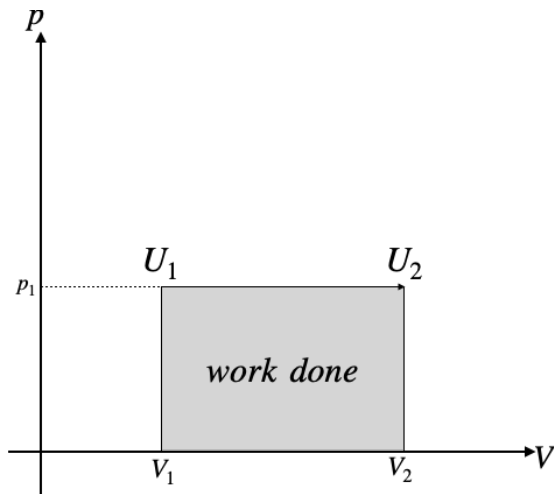
An increase in volume means work done on gas is negative

3.2 pressure-volume graphs

- Internal energy U is dependent on state and change in internal energy
- ΔU is independent of path taken
- Work done W is path dependent, and is the area under the P-V curve

3.3 Isobaric process

Volume changes at constant pressure. Area under curve is rectangular and magnitude of work done is $p\Delta V$



Isobaric expansion

Since volume increases, work done on the gas is negative
 Since

$$T \propto pV$$

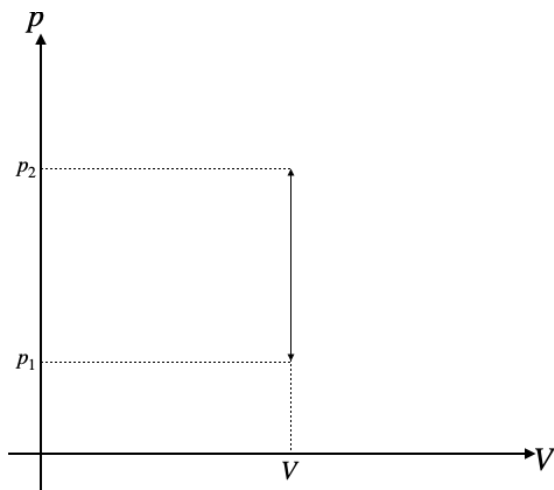
Temperature increases, and hence

$$\Delta U > 0$$

Hence heat is transferred into the system

3.4 Isovolumetric processes

Pressure changes without a change in volume



Isovolumetric process

Since V is constant, $W = 0$

$$\Delta U = Q + 0, \Delta U = Q$$

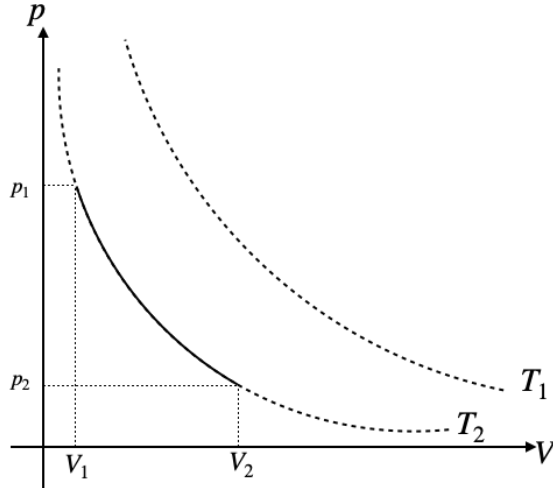
For an increase in pressure,

$$\Delta U > 0$$

$$Q > 0$$

3.5 Isothermal Process

For a system at constant temperature, and heat exchange happens slowly, such that pressure and volume changes occur without a change in temperature



Isothermal expansion

Along each isotherm, T constant, hence

$$\Delta U = 0$$

$$0 = Q + W$$

For an expansion, work is done by the system, hence

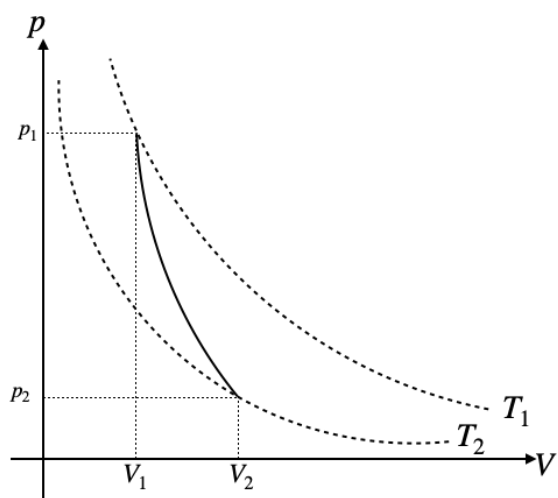
$$W < 0, \text{ hence } Q > 0$$

3.6 Adiabatic Process

When a system undergoes a change in pressure and volume with no heat being supplied to or lost from the system

This could happen if

- system is insulated
- the change in pressure and volume happens rapidly and hence no heat exchange with the surrounding occurs



For an expansion

$$W < 0$$

pressure decreases, T decreases, hence

$$\Delta U < 0$$