# UNIT 1: THERMODYNAMICS

Thermodynamics:- is the branch of science that studies energy relationship involving heat, mechanical work and energy transfer. These relationships have vital importance in the study of energy conversion devices such as heat engines and refrigerator.

## Atoms and moles

Atom:- is the smallest particle of an element capable of taking part in a chemical reaction.

Mole:- One mole (mol) of a substance is that contains as many particles(atoms, molecules, ions, or other particles) as there are atoms in 12g (0.012kg) of carbon-12 isotope.

Avogadro's number $N_A = 6.02\times10^{23}$particles/mol.

- ❖ One mole of helium gas contains $6.02\times10^{23}$ atoms of helium. One mole of water contains $6.02\times10^{23}$ molecules of water. That is $6.02\times10^{23}$ atoms of oxygen and $1.204\times10^{23}$ atoms of hydrogen.
- The relationship between number of moles (n), number of particles (N) and Avogadro's number ($N_A$) is:-

$$n = \frac{N}{N_A}$$

Molar mass:- is mass of 1 mole of substance. 1 mole of Carbon-12 has a molar mass of 12g= 0.012kg.
1 mole of Uranium-238 has a molar mass of 238g=0.238kg

- The relationship between mass of substance (m), number of moles (n), and molar mass (M) is:-

$$n = \frac{m}{M}$$

From the above relations, mass of each particle ($m_{pa}$) can be calculated using:

$$m_{pa} = \frac{m}{N} \quad \text{Or} \quad m_{pa} = \frac{M}{N_A}$$

Example

1. A sample of pure carbon-12 contains 4.2 moles of atoms. Calculate
   a) the number of atoms in the sample. **Ans**. $N=2.53\times10^{24}$atoms.
   b) mass of the sample. **Ans**. m= 0.0504kg, c) mass of each carbon-12 atom. **Ans**. $m_{pa}= 2\times10^{-26}$kg.
2. A sample of pure water contains 0.36kg. Determine
   a) the number of moles. **Ans**. n=20moles, b) the number of molecules of water. **Ans**. $N=1.204\times10^{25}$.

Exercise

1. Find the mass of a nitrogen molecule, (M=28g/mol). **Ans**. $m_{pa}=4.65\times10^{-26}$kg
2. How many helium atoms are there in 2g of helium if M=4g/mol? **Ans**. $N=3.01\times10^{23}$atoms.
3. Find the number of particles (N) and number of moles (n) from the given table.

| N | n |
|---|---|
| | 3.0 |
| $2.4\times10^{23}$ | |
| | 0.08 |
| $4.5\times10^{25}$ | |

Thermal equilibrium and temperature

In solids, particles are vibrating. In liquids and gases, the particles are moving freely. In all cases, the particles have kinetic energy; this causes them to collide with their neighbors. As a result, energy is distributed throughout the substance. The particles in the hotter body have more kinetic energy than those in the colder body. So there is a transfer of thermal energy from the hotter body to the colder one.

Thermal equilibrium:-is a situation in which *two objects would not exchange energy by heat or electromagnetic radiation* if they were placed in thermal contact.

Temperature:- is the *measure of the average random kinetic energy of particles in a body*, and is used to determine which direction there will be a net energy flow when two bodies are close to one another.

Zeroth law of thermodynamics:-states "If two bodies A and B are separately in thermal equilibrium with a third body C, then A and B are in thermal equilibrium with each other as well."

Two objects in thermal equilibrium with each other are at the same temperature.

Steady state:- is a situation that is not changing with time.

## Thermodynamic temperature scale

An international conference held in 1947 decided that the absolute temperature scale that should be used to be the thermodynamic, or ideal gas, temperature scale measured in Kelvin (K).

Absolute zero, *temperature at which all random motion of particles in a substance ceases*, is defined as zero (0) K.

Triple point of water, *the temperature at which all three states of water can coexist*, is defined as 273.16K.

$T(K) = T(^0C) + 275.15$

| | Absolute temp ( K ) | Celsius temp ($^0$C) |
|---|---|---|
| Absolute zero | 0.00 | – 273.15 |
| Triple point of water | 273.16 | 0.01 |
| Ice point | 273.15 | 0.00 |
| Steam point | 373.15 | 100.00 |
| Room temperature | 293.00 | 20.00 |

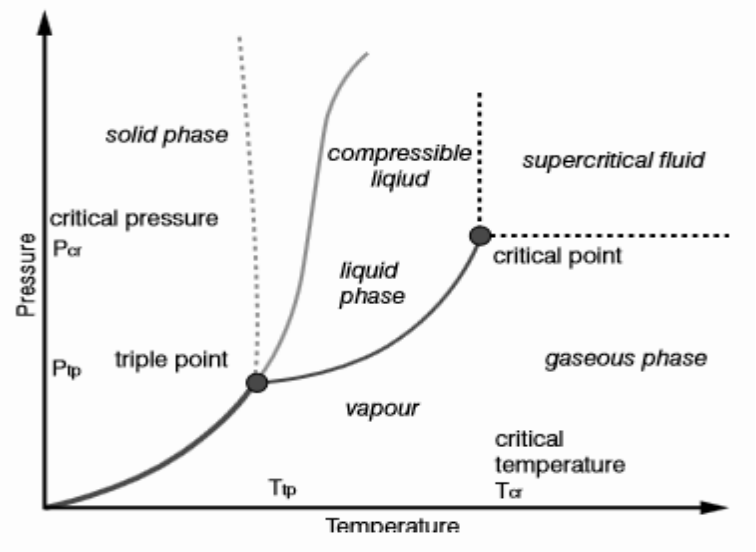
Exercise

1. Convert the following to degree Celsius
   a) 4.25K. **Ans**. –268.9$^0$C, b) 1340K. **Ans**. 1066.85$^0$C
2. Convert the following to Kelvin
   a) –39$^0$C. **Ans**. 234.15K, b) –270.42$^0$C. **Ans**. 2.73K
3. Temperature of a body is a measure of the
   A) heat content of a body.
   B**)** average molecular kinetic energy.
   C) average pressure in a gas.
   D) heat of vaporization of a liquid.
4. The zeroth law of thermodynamics states that:
   A**)** two bodies that are separately in thermal equilibrium with a third body must be in thermal equilibrium with each other.
   B) the increase in thermal energy of a system is equal to the sum of the energy entering the system through heating, and the work done on the system.
   C) no process is possible in which there is an overall decrease in the entropy of the universe.
   D) no process or cycle is perfectly reversible and no refrigerator or heat engine can be perfectly efficient.
5. Two bodies that are separately in thermal equilibrium with a third body must be in thermal equilibrium with each other. This statement is statement of:
   A) the first law of thermodynamics.
   B) the zeroth law of thermodynamics.
   C) the second law of thermodynamics.
   D) the third law of thermodynamics.
6. Three metals are in contact and are in thermal equilibrium. The metals have different specific heat capacities. What can be concluded about the temperature of the metals?
   A) Since they have different specific capacity, they must have different temperature at thermal equilibrium.
   B**)** They must have the same temperature at thermal equilibrium.
   C) They must have different internal energy.
   D) They must have different kinetic energy.

## Phase of matter

A solid phase is the state in which the substance maintains a fixed shape and a fixed volume, whereas the liquid phase is a state in which the substance can change its shape to take the shape of its container.

* Changing the pressure or temperature of a substance will affect its phase.




***Phase diagram showing different states of matter***

$P_{trp}$ is triple point of pressure; $P_{cr}$ is critical pressure.

$T_{trp}$ is triple point of temperature; $T_{cr}$ is critical temperature.

Critical:- denote a point of transition from one state to another.

Triple point:- is the specific temperature and pressure where all three states of matter are able to exist in thermal equilibrium.

Critical point (critical state):- is where the critical temperature and critical pressure of a substance meet.Above this point clear phase boundaries cease to exist.

- Above the critical temperature it is not possible to form a liquid, regardless of any change in pressure.
- Critical point is different from the boiling point of a substance. The boiling point of a substance is the point at a standard atmospheric pressure.

The lower the pressure, the lower the boiling point.

The critical point occurs only at one specific temperature and pressure.

Critical Constants

| Substance | Critical temp (K) | Critical pressure (Pa) | Critical Volume ($m^3$/mole) | Critical density ($kg/m^3$) |
|---|---|---|---|---|
| Helium | 5.3 | $2.29\times10^5$ | $57.8\times10^{-6}$ | 69.3 |
| Hydrogen (normal) | 33.3 | $13\times10^5$ | $65.0\times10^{-6}$ | 31.0 |
| Nitrogen | 126.2 | $33.9\times10^5$ | $90.1\times10^{-6}$ | 331.0 |
| Oxygen | 154.8 | $50.8\times10^5$ | $78.0\times10^{-6}$ | 410.0 |
| Ammonia | 405.5 | $112.8\times10^5$ | $72.5\times10^{-6}$ | 235.0 |
| Carbon dioxide | 304.2 | $73.9\times10^5$ | $94.0\times10^{-6}$ | 468.0 |
| Water | 647.4 | $221.4\times10^5$ | $56.0\times10^{-6}$ | 320.0 |

## Work, heat and the first law of thermodynamics

The internal energy of a system is the sum of the random distribution of kinetic and potential energies associated with the molecules within that system. Within an ideal gas, there are no intermolecular forces except during collisions, so ***the internal energy is equal to the sum of random kinetic energies of the particles only.***

*The first law of thermodynamics:- " *Heat added to a system is equal to the sum ofwork done by the system and the increase in the internal energy of the system."*

$\Delta Q = \Delta U + W$

OR $\Delta Q = \Delta U + P\,\Delta V$

Where $\Delta Q$ is the heat supplied
$\Delta U$ is the increase in internal energy
W is the work done by the system
P is pressure
$\Delta V$ is change in volume

Sign Convention

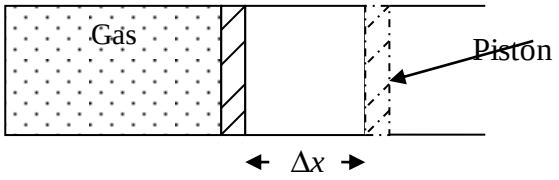
- $\Delta Q$ is +Ve when heat is supplied to the systems; – Ve when the system loses heat.
- $\Delta U$ is +Ve when it increases; –Ve When it decreases.
- W is +Ve if the system does work on its surroundings; – Ve if work is done on the system.

When heat is added to a gas inside a cylinder, it pushes a frictionless piston as it expands.
If the displacement $\Delta x$ is small, the pressure P of the gas is can be assumed to be constant.
The force that the gas exerts on the piston is:

$F = PA$

Thus, the work done on the piston

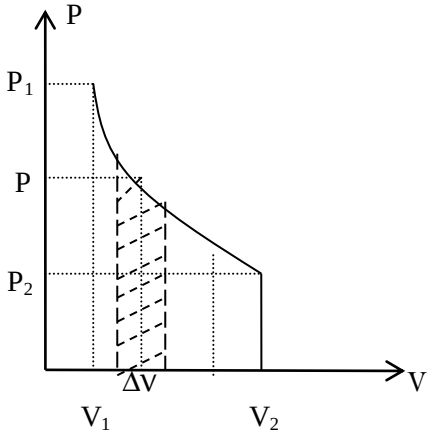
$W = F(\Delta x)$
$= PA\Delta x$
$= P\Delta V$




Consider the P-V diagram of an ideal gas shown below. From the graph, the work done by the gas as it expands from $V_1$ to $V_2$ cannot be directly determined as $P\Delta V$, because both pressure and volume of the gas change. However, for small change $\Delta V$, the pressure of the gas can be taken to be constant, say P.

Therefore, the work done by the gas for this expansion is $P\Delta V$ (*area of the small shaded strip of the graph*.)

**The total work done is the area under the P-V diagram** (total shaded region)

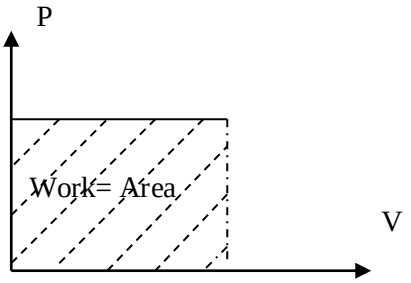



When one of the variables is kept constant, it becomes easier to apply the first law for the process. The following are such processes.

Note: When work is done
* by the gas, the arrow is pointing to the right.
*on the gas, the arrow is pointing to the left.

*I*) Isobaric Process:- is a thermodynamic process that occurs at a constant pressure. This can be attained by slowly adding heat to the system.

W= PΔV




Example

1. The pressure of a gas is maintained at 8000Pa while a 52J of heat is added. If the piston of cross-sectional area $0.1m^2$ is pushed outwards by 4cm, what is
   a) the work done by the gas? **Ans**. W= 32J. b) the change in internal energy? **Ans**. ΔU= 20J
2. When a $5\times10^4$J of heat is added to an ideal gas in a cylinder, it expands isobarically at $P=2\times10^5$Pa, from a volume of$0.4m^3$ to $0.6m^3$.Calculate:
   a) work done by the gas. **Ans**. $W = 4\times10^4$J,
   b) the change in internal energy. **Ans**. $\Delta U=10^4$J
3. What happened to the temperature of the gas in question 2 above; increase, decrease or remain constant?

Exercise

1. A gas pushes a piston of cross-sectional area $100cm^2$ through a distance of 10cm with a pressure of 100kPa.What is the work done by the gas? **Ans**. W= 100J
2. If 100J of heat is added to a system that does 40J of external work, by how much is the internal energy of the system raised? **Ans**. ΔU=60J
3. In a certain process of an ideal gas, 4000J of work is done on the system and 4900J of heat is extracted from the system.
   *a*) Calculate the change in internal energy. **Ans**. ΔU= – 900J. b) What happens to the temperature?
4. A gas under a pressure of $5\times10^5$Pa is heated to expand from $10cm^3$ to $30cm^3$. If the pressure is held constant while 40J of heat is added, what is
   a) the work done by the gas? **Ans**. W=10J. b) the change in internal energy? **Ans**. ΔU=30J
5. A cylinder of cross-sectional area $20cm^2$ contains a gas at a pressure of $2\times10^5$Pa. When 300J of heat is added, the piston moves outward by 20cm. What is
   a) work done by the gas? **Ans**. W=80J. b) the change in internal energy? **Ans**. ΔU=220J

## *Questions from national exam*

1. The volume of a gas goes from $0.4m^3$ to $0.6m^3$ while the pressure remains constant at $2\times10^5$Pa. What is the work done by the gas?

   A) $-2\times10^4$J  B) $2\times10^4$J  C) $-4\times10^5$J  D) $4\times10^4$J

2. A gas is enclosed in a container fitted with a piston of cross-sectional area $0.1m^2$. When the pressure of the gas is maintained at 8000Pa while heat is slowly added, the piston is pushed up a distance of 4cm. If 42J of heat is added to the system during expansion, then what is the change in internal energy of the system in joules?

   A) 10  B) 12  C) 8  D) 21

3. A gas is compressed at a constant pressure of $8\times10^4N/m^2$ from a volume of $9\times10^{-3}m^3$ to a volume of $3\times10^{-3}m^3$.In the process 400J of heat energy flows out of the gas. What are the work done on the gas and the change in internal energy of the gas? **Ans**. W= –480J, $\Delta$U= 80J

   A) –567J, –167J  B) –560J, –160J  C) – 589J, –189J  D) –540J, –140J

4. What does a curve drawn between two points on P-V diagram represent?

   A) The state of the system.  C) Work done in a cyclic process.

   B) A thermodynamic process.  D) Work done on or by the system.

5. Which one of the following statements is necessarily true about the first law of thermodynamics?

   A) The amount of heat transferred appears as change in internal energy only.

   B) The amount of heat transferred is related to internal energy and work done.

   C) Work done is equal to the amount of heat transferred.

   D) Internal energy is equal to the work done.

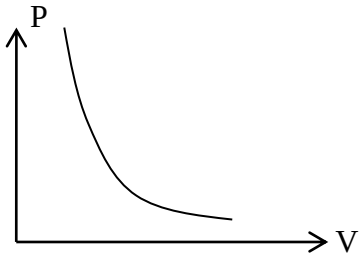
*II*)Adiabatic process:- is a process in which **no heat transfer into or out of a system**. It is practically impossible to have a perfectly adiabatic process. However, a very quick process can be taken as an adiabatic.

For adiabatic process, $\Delta Q= 0$

The first law for adiabatic takes a form

$W_{adia}= -\Delta U$

- When a gas expands adiabatically,
  W is +Ve and $\Delta$U is –Ve
- When a gas is compressed adiabatically,
  W is –Ve and $\Delta$U is +Ve




The temperature of a gas:

***decreases** when it undergoes **adiabatic expansion**.

***increases** when it undergoes **adiabatic compression**.

Exercise

1. How can the temperature of a gas
   a) be raised without heat flowing to it?  b) be decreased without heat flowing from it?
2. What happens to the temperature of air enclosed in a pump,
   a) when it is compressed?  b) when it undergoes expansion?
3. An ammonia gas expands rapidly and pushes a frictionless piston by a distance of 5cm. If the pressure of the gas remains constant at 130kPa, what happens to the temperature of the ammonia gas? Hint: $\Delta U = m_{amm}c_{amm}\Delta T$
   ( $m_{amm}$= 650mg, $c_{amm}$=2.2kJ/kg.k, $A_{pist}= 3\times10^{-3}m^2$) **Ans**. $\Delta T= -13.6K$

4. A gas is allowed to expand adiabatically. In doing so the gas does 850J of work.
   a) How much heat flowed out of the gas?
   b) What is the change in internal energy?
   c) will its temperature rise or fall?

*III*) Isothermal process:- is a process in which ***temperature of the gas remains constant***.

During isothermal process ΔU= 0. Why?

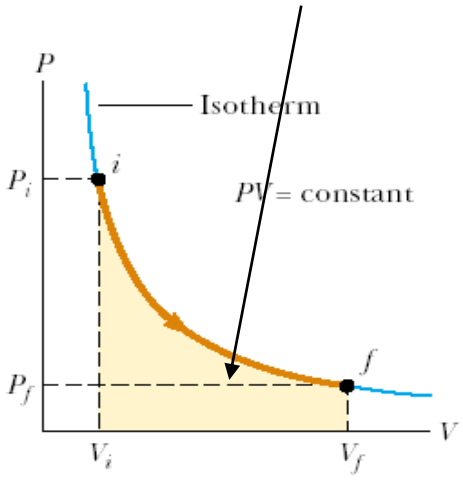
The first law for isothermal process takes a form

$$\Delta Q = W_{isoth}$$

*The **work done by/ on the gas at constant temperature T as it expands / is compressed from $V_i$ to $V_f$** is given by*

$$W = nRT\ \ell n\ \frac{V_f}{V_i}$$

Area under the curve= Work done




♦When the gas **expands** isothermally, $V_f > V_i$, then $\ell n\ \frac{V_f}{V_i} > 0$ and **the work done is +ve**;ΔQ is also +Ve

♦ When the gas **is compressed** isothermally, $V_f < V_i$, then $\ell n\ V_f/V_i < 0$ and **the work done is -ve**;ΔQ is also –Ve.

**A gas that *expands* isothermally *does work* equal to the heat that flows into it.**
**A gas that is *compressed* isothermally *gives out heat* that is equal to the work done on it.**

Example

1. A gas is compressed to half its initial volume isothermally. During the process 18000J of work is done on the gas.
   a) What is the change in internal energy of the gas? **Ans**. ΔU=
   b) Calculate the heat added to or removed from the gas.
2. A 0.24 mole gas, at a temperature of 310K, expands until the volume of the gas is doubled.
   a) What is work done by the gas? **Ans**. W= 428.7J
   b) How much heat is added to the gas for this process? **Ans**.

| Given | Required | Soln |
|---|---|---|
| $n$ = 0.24 mol | a) W= ? | a) $W = n\ RT\ \ell n\ \frac{V_f}{V_i}$ , $W = 0.24 \times 8.314 \times 310\ \ell n \frac{2V_i}{V_i}$ |
| T = 310K | b) ΔQ =? | = 428.7J |
| $V_f = 2\ V_i$ | | b)ΔQ = W |

3. A balloon contains 5moles of monatomic ideal gas. As energy it absorbs heat from the Sun, the volume increases by 25% at a constant temperature of $27C^0$ . Find
   a) the work done by the gas in expanding the balloon. **Ans**. $W = 2.78 \times 10^3 J$
   b) the thermal energy *Q* transferred to the gas.

*Questions from national exam*

1. A sample of gas is expanded to twice its original volume of $1m^3$ in a quasi-static pressure for which P= αV, with$\alpha=5\times 10^5 N/m^5$. How much work was done by the expanding gas?

   A**)** 0.75MJ  B) 1.0MJ  C) 7.5MJ  D) 1.5MJ

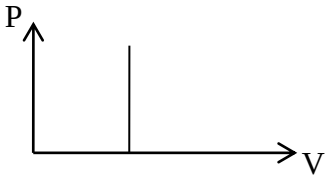
2. An ideal gas undergoes an isothermal process starting with a pressure of $2\times10^5$ Pa and a volume of 6 $cm^3$. Which one of the following might be the pressure and volume of the final state?

   A) $4\times10^5$ Pa and 4 $cm^3$  C) $5\times10^5$Pa and 3 $cm^3$

   B**)** $4\times10^5$Pa and 3 $cm^3$  D) $10^5$Pa and 10 $cm^3$

IV) Isochoric (Isovolumetric) process:- is a process in which **volume of the gas remains constant**.

For isochoric process, **no work is done on, or by the system**.




W= 0 because PΔV= 0

The first law for isochoric process takes a form:

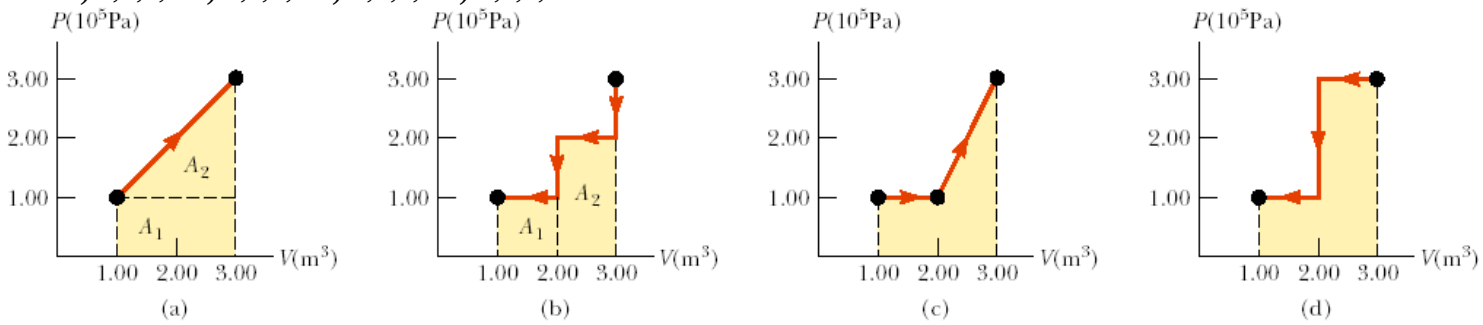
ΔQ= ΔU

*The amount of heat transferred appears as change in internal energy only.*

Example

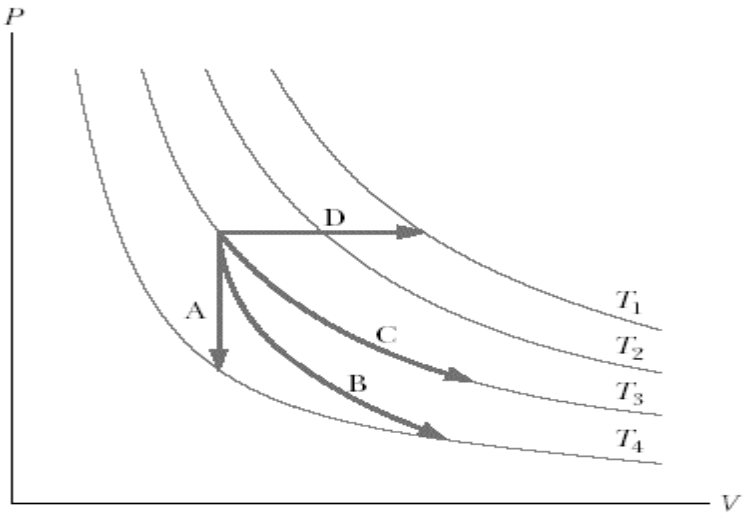
1. If 100J of heat is added to a system that does no external work, by how much is the internal energy of the system raised?
2. A 6000J of heat is added to water in a rigid container. Calculate the change in internal energy of the water.
3. One mole of an ideal gas is contained in a cylinder with a movable piston. The initial pressure, volume, and temperature are $P_i$, $V_i$, and $T_i$, respectively. Find the work done on the gas for the following processes and show each process on a *PV* diagram:
   a) An isobaric compression in which the final volume is half the initial volume.
   b) An isothermal compression in which the final pressure is four times the initial pressure.
   c) An isovolumetric process in which the final pressure is three times the initial pressure.
4. By visual inspection, order the *PV* diagrams shown in figure below from the most negative work done on the system to the most positive work done by the system.

   a) a,b,c,d b) a,c,b,d c) d,b,c,a d) d,a,c,b



5. Identify the paths A, B, C, and D in the following figure as isobaric, isothermal, isovolumetric, or adiabatic.

For path B, $\Delta Q = 0$.

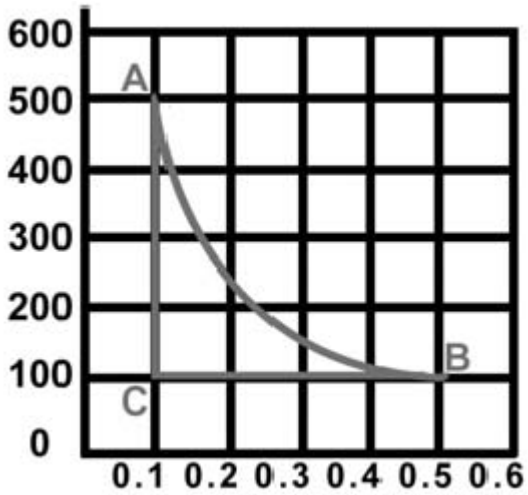



6. Study the following diagram. What is the process

a) between the points B and C?

b) between the points C and A?

c) Does the gas expand adiabatically or isothermally between the points A and B?



## Molar heat capacities of ideal gas

*The molar heat capacity of an ideal gas*: is **the amount of heat required to raise the temperature of one mole of a gas by $1^0$C or by 1K**.

The molar heat capacity of a gas at constant volume is:

$C_v = \frac{\Delta Q_v}{n\Delta T}$ or $\Delta Q_v = nC_v\Delta T$ (1)

The molar heat capacity at constant pressure is:

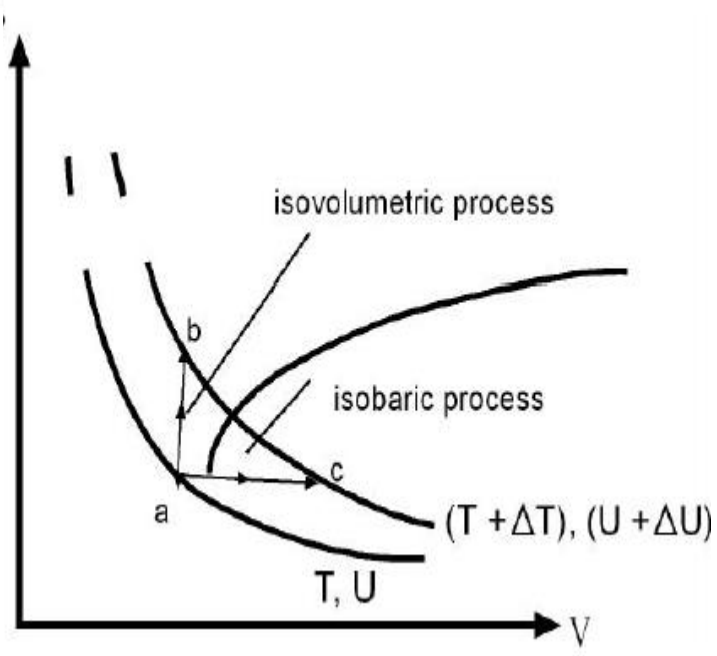
$C_p = \frac{\Delta Q_p}{n\Delta T}$ or $\Delta Q_p = nC_p\Delta T$ (2)

*For the isovolumetric process* **a** to **b**, the first law

$\Delta Q_v = \Delta U + W$ is reduced to

$\Delta Q_v = \Delta U$ because $\Delta V = 0$

$nC_v\Delta T = \Delta U$ (3)




*For isobaric process* **a** to **c**, the first law

$\Delta Q = \Delta U + P\Delta V$ becomes

$nC_p\Delta T = nC_v\Delta T + P\Delta V$

Using ideal gas equation $P\Delta V = nR\Delta T$

$nC_p\Delta T = nC_v\Delta T + P\Delta V$ becomes

$nC_p\Delta T = nC_v\Delta T + nR\Delta T$ Where R= 8.314 J/mol.K universal gas constant.

Dividing both sides by $n\Delta T$, we get

$C_p - C_v = R$ Was first derived by Robert Mayer in 1843 and is called **Mayer's equation**.

It holds for any ideal gas (one for which there is no intermolecular potential energy.)

*It takes less heat to produce a given temperature change at constant volume than it does at constant pressure. Because at constant pressure all of heat does not go into changing temperature; some of the heat goes into doing work. On the other hand, at constant volume no work is done, so all the heat goes into changing the temperature.*

Example

1. What are the units of $C_p$ and $C_v$?
2. Is $C_p$ greater than, smaller than or equal to $C_v$? Explain.
3. A cylinder contains 3 moles of helium gas at a temperature of 300 K. If $C_V$=12.5 J/mol .K & $C_p$ = 20.8J/mol. K
   How much energy must be transferred by heat to the gas for its temperature to increase to 500 K?

a) at constant volume? b)at constant pressure ?

| Given | Required | Soln |
|---|---|---|
| $n$ = 3moles | a ) $\Delta Q_v$ = ? | a) $\Delta Q_v = n\,C_v\Delta T = 3\times 12.5\times 200 =$ 7500 J |
| $T_i$ = 300K | b) $\Delta Q_p$ =? | b) $\Delta Q_p = n\,C_p\Delta T = 3\times 20.8\times 200 =$ 12480J |
| $T_f$ = 500K | | |

Note that $\Delta Q_p$ is larger than $\Delta Q_v$, due to the transfer of energy out of the gas by work in the constant pressure process.

4. Oxygen gas has $C_p$= 29.37J/mol.K. Calculate
   a) the amount of heat that must be supplied to 2 moles of the gas to increase its temperature from $10^0$C to $40^0$C at constant volume.
   b)the change in internal energy of the gas. **Ans**. ΔU= 1263.6J

| Given | Required | Soln |
|---|---|---|
| $C_p$= 29.37J/mol.K | a) $\Delta Q_v$= ? | a) $\Delta Q_v = n\,C_v\Delta T$ But $C_v = C_P - R$= 29.37– 8.31= 21.06J/mol. K |
| $n$ = 2mol | b) ΔU= ? | = 2×21.06×30 = 1263.6J |
| ΔT = 30K | | b) At constant volume $\Delta U = \Delta Q_v$ = 1263.6J |

5. Three moles of ideal gas expands at constant pressure, whilst the temperature of the gas increases from $30^0$C to $35^0$C.The internal energy of the gas increases by 187.2J during the process. Calculate $C_p$ for the gas.
   **Ans**. $C_p$=

| Given | Required | Soln |
|---|---|---|
| $n$ = 3mol | $C_p$= ? | $C_p = C_v + R$ But $C_v = \frac{\Delta U}{n\Delta T} = \frac{187.2J}{3\times 5K}$ = 12.48J/K |
| ΔT= 5K | | = 12.48 + 8.31 |
| ΔU = 187.2J | | = 20.79J/mol.K |

6. When heating one mole of certain gas at constant volume, an energy transfer of 124.71J produces an increase in temperature of 10K. What temperature increase there would be if the same amount of gas was heated in the same way at constant pressure? Take $C_v$ = 12.471J/mol. K and $C_p$= 20.785J/mol. K

| Given | Required | soln |
|---|---|---|
| $\Delta Q_v = \Delta Q_p$= 124.71J | $\Delta T_p$= ? at constant pressure | The amount of heat supplied is the same |
| $\Delta T_v$= 10K at constant volume. | | $\Delta Q_v = \Delta Q_p$ |
| | | $C_v n\Delta T_v = C_p n\Delta T_p$ |
| | | $\Delta T_P = \frac{C_v}{C_p}\Delta T_v = \frac{12.471}{20.785}\times 10K$ = 6K |

## Adiabatic Process Of Ideal Gas

For adiabatic process of ideal gas

$\Delta U = nC_v\Delta T$ and $W = P\Delta V$

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

$\Delta U = -W$

OR $nC_v\Delta T = -P\Delta V$ (1)

Since the gas is ideal, $PV = nRT$ becomes

$P\Delta V + V\Delta P = nR\Delta T$ for small changes

OR $\Delta T = \frac{1}{nR}(P\Delta V + V\Delta P)$ (2)

Substituting eq( 2 ) into eq ( 1 ) we get $C_vP\Delta V + C_vV\Delta P = -RP\Delta V$

OR $C_vP\Delta V + RP\Delta V = -C_vV\Delta P$

$(C_v + R)P\Delta V = -C_vV\Delta P$

$C_pP\Delta V = -C_vV\Delta P$

$$\frac{C_p}{C_v}\frac{\Delta V}{V} = -\frac{\Delta P}{P} \Longrightarrow \gamma\frac{\Delta V}{V} = -\frac{\Delta P}{P} \quad \text{Where } \gamma = \frac{C_p}{C_V}$$

Using integral calculus, this gives

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

This is a relation that holds between P and V for which a reversible adiabatic process of an ideal gas ($\gamma$ remains constant)

- What is the unit of $\gamma$?
- Is $\gamma$ greater than, smaller than or equal to one?

For *monatomic gas* $C_V = \frac{3}{2}R$, $C_P = \frac{5}{2}R$ and $\gamma = 5/3 = 1.67$

For *diatomic gas* $C_V = \frac{5}{2}R$, $C_p = \frac{7}{2}R$ and $\gamma = 7/5 = 1.4$

There is ***no simple regularity for polyatomic gases***.

*The values of $\gamma$ for different real gases*

| Types of gas | Gas | $\gamma$ |
|---|---|---|
| Monatomic | He | 1.67 |
| | Ar | 1.67 |
| Diatomic | $H_2$ | 1.41 |
| | $N_2$ | 1.40 |
| | $O_2$ | 1.40 |
| | CO | 1.40 |
| Polyatomic | $CO_2$ | 1.30 |
| | $SO_2$ | 1.29 |
| | $H_2S$ | 1.33 |
| | $CH_4$ | 1.31 |

Example

1. Air, with $\gamma = 1.40$, at $20^0$C in a cylinder is compressed from initial pressure of $10^5$Pa and volume of 800cm$^3$ to a volume of 60cm$^3$. If the compression is adiabatic, calculate
   a) the final pressure. **Ans**. $P_2$= 3757630Pa. b) the final temperature. **Ans**. $T_2$= 826K
2. A gas, with $\gamma$ = 1.4, under a pressure of $10^5$Pa and temperature of 300K is compressed adiabatically to 1/16 times its original volume. Calculate:
   a) the final pressure. **Ans**. $P_2$= 4850290Pa. b) the final temperature. **Ans**. $T_2$= 910K

Exercise

1. Prove that a) $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$, b) $T_1P_1^{\frac{1-\gamma}{\gamma}} = T_2P^{\frac{1-\gamma}{\gamma}}$. Hint: Use the gas equation PV=$n$RT
2. A cylinder contains oxygen gas at 280K occupying a volume of 0.25m$^3$. The gas is compressed adiabatically to 0.14m$^3$. Find the increase in temperature of the gas. **Ans**. $T_2$ = 353K, $T_2 - T_1$= 73K
3. A certain volume of helium gas at 15K is expanded adiabatically until its volume is tripled. Calculate the temperature of the gas immediately after expansion. **Ans**. $T_2$= 7.2K
4. A gas occupies a volume of 4.4 ℓit at a pressure of 1.4kPa and temperature 300K. It is compressed adiabatically to a volume of 0.76 ℓit. If $\gamma = 1.4$, find
   a) the final pressure. **Ans**. $P_2$= 16361.4Pa. b) the final temperature. **Ans**. $T_2$= 606K
5. A monatomic gas in a cylinder suddenly compressed to one- fifteenth its original volume and causes a rise in temperature. If its initial pressure and temperature are $10^5$Pa and $27^0$C respectively. Find,
   a) final pressure. **Ans**. $P_2 = 9.2\times10^6$Pa. b) final temperature. **Ans**. $T_2$= 1840K
6. Which one of the relation is wrong when an ideal gas is subjected to an adiabatic process?

   A) $PV^{\gamma}$= constant B) $PV^{\gamma}$ = constant C) $TV^{\gamma-1}$ = constant D) $TP^{\left(\frac{1}{\gamma}-1\right)}$ = constant

# Kinetic theory of ideal gas

The kinetic theory of gases applies only to ideal gases that have the following properties.

*i*) The internal energy of the gas is due to the random kinetic energies of particles only. There is no potential energy component. There is no interaction between particles or between particles and the wall except during collisions.

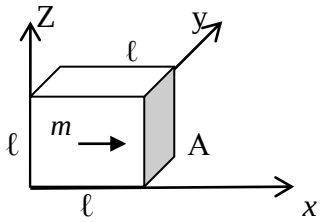
*ii*) Collisions of the molecules with one another and with the wall are perfectly elastic; there is no loss of kinetic energy during collision.

*iii*) The volume occupied by the particles is negligible compared to the volume of the gas as a whole.

*iv*) The distribution of velocities of particles is random. That is, the average distribution of velocities over time is the same in all directions.

*v*) Basic laws of dynamics can be applied to all collisions.

Consider a cube containing **N** molecules. If a molecule of mass **m** moving in the *x*- direction collides with the face **A** of the cube.




$\Delta P = 2mv$ (change in momentum)

$\Delta t = \frac{2\ell}{v}$ (total time taken by the molecule)

The force exerted by one molecule on the wall is

$$F = \frac{\Delta P}{\Delta t} = \frac{2mv}{2\ell / v} \Longrightarrow F = \frac{mv^2}{\ell}$$

For N molecules $F_{tot}$ is $F_{tot} = N\frac{mv^2}{\ell}$

Remember that only one-third of the molecules in the cube are moving in the *x*-direction.

*The force exerted on one face of the cube is

$$F = \frac{1}{3}N\frac{mv^2}{\ell}$$

*The pressure of the gas molecules on the face is

$$P = \frac{F}{A}$$

$$= \frac{1}{3}N\frac{mv^2}{\ell}/\ell^2$$

$$= \frac{1}{3}N\frac{mv^2}{\ell^3}$$

$$P = \frac{1}{3}N\frac{mv^2}{V}$$

Or $PV = \frac{1}{3}Nmv^2 = \frac{2}{3}N(\frac{1}{2}mv^2)$

$PV = \frac{2}{3}N(K.E_{av})$ Kinetic theory equation

Where m is mass of one molecule

N is number of molecules

*v* is speed of the molecule

V is volume of the cube

$N_A$ is **Avogadro's** number

$k = R/N_A = 1.381\times10^{-23}$ J/K **Boltzmann's** constant

From PV= nRT

$$PV= \frac{N}{N_A} RT$$

Therefore $\frac{2}{3} N( K.E_{av}) = \frac{N}{N_A} RT$

The average kinetic energy of

- **one molecule** of gas is : $K.E_{Av}= \frac{3}{2} kT$
- **N molecules** of gas is: $K.E_{Av}= \frac{3}{2} N k T$
- **one mole** of gas is: $K.E_{Av}= \frac{3}{2} N_A kT$ Or $K.E_{Av}= \frac{3}{2} RT$
- ***n* moles** of gas is: $K.E_{Av}= \frac{3}{2} nRT$ Or $K.E_{Av}= \frac{3}{2} \frac{N}{N_A} RT$

The average kinetic energy of the molecules in an ideal gas is proportional to the absolute temperature of the gas.

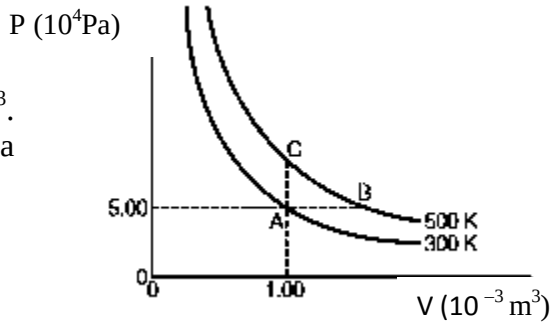
Example

1. A cylinder contains oxygen gas at a temperature of $27^0$C and pressure of 1atm in a volume of 100ℓit. The gas is compressed to a volume 80ℓit. If the new temperature is $30^0$C,
   a) how many moles of oxygen gas are in the cylinder? **Ans**. n= 4moles
   b) what is the new pressure of the gas? **Ans**. $P_2$= 1.26atm
2. A cylinder contains an ideal gas at a temperature of 840K. Calculate:
   a) the average kinetic energy of one molecule of the gas. **Ans**. $K.E_{Av}= 1.74\times10^{-20}$J
   b) the internal energy of one mole of the gas. **Ans**. U= $K.E_{tot}$= 10475J
3. A tank used for filling helium balloons has a volume of 0.3 $m^3$ and contains 2.0 mol of helium gas at 20 °C.
   a) What is the total translational kinetic energy of the gas molecules? **Ans**. 7308J
   b) What is the average kinetic energy per molecule? **Ans**. $6.065\times 10^{-21}$J

Exercise

1. A roomful of air has the dimensions 4m×3m×3m. If the temperature and pressure are $27^0$C and 100kPa respectively, calculate the number of molecules of air in the room. **Ans**. No of molecules= $8.7\times10^{26}$
2. An ideal gas is sealed within a container at a temperature of $17^0$C and a pressure 101 kPa. The container is heated until the temperature of the gas reaches $100^0$C. A valve in the container is then opened to allow the gas to escape until the pressure falls back to 101kPa at $100^0$C. Calculate
   a) the pressure in the gas just before the valve is opened. **Ans**. P= 129907Pa
   b)the percentage of mass of the gas that was lost as a result of opening the valve. **Ans**. 22% the remaining 78%
3. Calculate the internal energy of one mole of nitrogen gas at a pressure of 50kPa occupying a volume of $5\times10^4 cm^3$. **Ans**. U= 3750J

4. The figure below shows curves relating P and V for a fixed mass of an ideal monatomic gas at 300K and 500K.




a) What is
*i*) the number of moles of the gas? **Ans**. *n*= 0.0201mol
*ii*) the volume of the gas at B on the graph? **Ans**. $V_B = 1.67\times10^{-3}m^3$.
*iii)* the pressure of the gas at C on the graph? **Ans**. $P_B$ = 83555.7 Pa

b) Calculate the total internal energy of the gas
*i*) at point A on the graph. **Ans**. $U_A = K.E_{tot}$= 75.2J
*ii*) at point B on the graph. **Ans**. $U_B = K.E_{tot}$= 125.3J
*iii*) at point C on the graph. **Ans**. $U_C = K.E_{tot}$= 125.3J

c) What is the work done from
*i*) A to C? **Ans**. W=
*ii*) A to B? **Ans**. W= 33.5J
*iii*) C to B? **Ans**. W = 42.85 J

d)What is the energy absorbed by the heating, ΔQ, from
*i*) A to C? **Ans**. ΔQ= ΔU= 50.1J
*ii*) A to B? **Ans**. ΔQ= 83.6J
*iii)* C to B? **Ans**.

## *Questions from national exam*

1. A cylinder contains 12ℓit of an ideal gas at $27^0$C and a pressure of 15atm. If the temperature is increased to $37^0$C and the volume is reduced to 8ℓit, what is the final pressure of the gas?
A) 11.625atm **B) 23.25atm** C) 34.875atm D) 46.5atm

2. A cylinder contains 8ℓit of an ideal gas at a temperature of 300K and at a pressure of 12atm. If the volume is increased to 10ℓit and the pressure is reduced to 4atm, what is the new temperature of the gas?
A) 115K B) 120K **C) 125K** D) 130K

3. Which of the following statements follows from kinetic theory of gases?
**A) The pressure of the gas is proportional to the average of square of molecular speed of particles.**
B) The molecules undergo inelastic collisions with each other and with the walls of the container.
C) The force between molecules of gas are strong at all times.
D) Newton's laws of motion is the consequence of kinetic theory of gases.

4. Which statement is NOT among the assumptions made in the kinetic theory of gases?
A) There is no interaction between particles or between particles and the wall except during collision.
B) Collisions between particles and between particles and walls are perfectly elastic.
C) The volume occupied by the particle is negligible compared to the volume of the gas as a whole.
D) The distribution of velocities of particles is uniform.

5. The temperature of a gas is due to
A) the kinetic energy of the molecules. C) the attractive force between the molecules.
B) the potential energy of the molecules D) the repulsive force between the molecules.

6. A given weight of gas has a temperature of $27^0$C and volume V. Keeping the pressure constant, the volume is increased to 3V by varying the temperature. What is the final temperature of the gas?
A) $81^0$C B) $546^0$C **C) $627^0$C** D) $900^0$C

## Root Mean Square Velocity

The mean square velocity of molecules:- is *the average of the sum of square of velocities of all the N molecules*.

$$\overline{v^2} = \frac{v_1^2 + v_2^2 + ... + v_N^2}{N}$$

In practical calculations, the root mean square velocity is used. The root mean square velocity ( $v_{rms}$ ) is given by

$$v_{rms} = \sqrt{\overline{v^2}}$$

Example

Given the following velocities: 300m/s, 400m/s, 500m/s, 600m/s, find

a) the mean square velocity. **Ans**. $\overline{v^2} = 215000 m^2/s^2$. b) the root mean square velocity. **Ans**. $v_{rms} = 464 m/s$

Dalton's Law of Partial Pressure:- states *" When two or more gases which do not interact chemically are present in the same container, the total pressure is the sum of the partial pressures."*

$$P = \sum P_i$$

Suppose we have a volume V that contains $n_1$ moles of gas with partial pressure $P_1$ and $n_2$ moles of gas with a partial pressure $P_2$ and if the gas mixture is in thermal equilibrium at a temperature T, then

$P_1V = n_1RT$ and $P_2V = n_2RT$

Prove that a) $P_1+P_2 = P$, b) $n_1+n_2 = n$, c) $P_1/P_2 = n_1/n_2$

Graham's Law of Diffusion: The rate of diffusion

a) at a fixed pressure is **inversely proportional to the square root of density ($\rho$ ) of the gas**

$$v_{rms} = \sqrt{\frac{3P}{\rho}}$$

b) at a fixed temperature is **inversely proportional to the square root of the molar mass ($M_m$) of the gas**

$$v_{rms} = \sqrt{\frac{3RT}{M_m}}$$

Example

1. Calculate the rate of diffusion ( $v_{rms}$ ) of nitrogen molecules at STP. ($\rho_{nit} = 1.251 kg/m^3$, $P = 1.01\times10^5 Pa$).

   **Ans**. $v_{rms} = 492 m/s$

2. Find the rate of diffusion for hydrogen molecule at a temperature of 3.5K. **Ans**. $v_{rms} = 209 m/s$

Exercise

1. For two different gases at the same temperature
   i) with molecular masses $m_1$ and $m_2$, the rate of diffusion $v_1$ *and* $v_2$, respectively: prove that $v_1^2/v_2^2 = m_2/m_1$
   *ii*) with densities $\rho_1$ and $\rho_2$, the rate of diffusions $v_1$and $v_1$, respectively: prove that $v_1^2/v_2^2 = \rho_2/\rho_1$
2. The rms speed of molecules of helium gas at 332K is 1440m/s. What is the rms speed of hydrogen gas at the same temperature and pressure? **Ans**. $v_H = 2036 m/s$
3. At what temperature $T_2$ will molecules of an ideal gas have twice $V_{rms}$ they have at $T_1$? **Ans**. $T_2 = 4T_1$
4. A container, at a temperature of 300K, has a volume of $0.01 m^3$ and there is 0.2mole of air in the container. Air contains approximately 80% nitrogen and 20% oxygen. Calculate the partial pressures of nitrogen and oxygen.
   **Ans**. $P_{nit} = 39907.2 Pa$ , $P_{oxy} = 9976.8 Pa$
5. Air at room temperature has a density of $1.29 kg/m^3$. Assume it to be entirely one gas, find the rate of diffusion. ($P = 10^5 Pa$) **Ans**. $v_{rms} = 482 m/s$

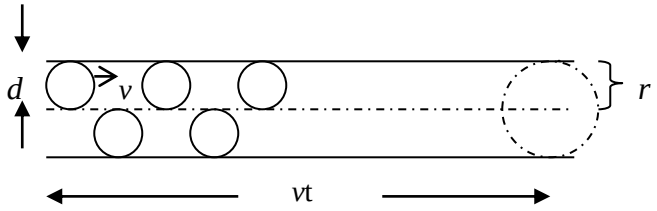
## *Questions from national exam*

1. Suppose the molecules of different masses are kept at the same temperature. Which one of the following statements is NOT true?
   A) Both remain at rest. C) The lighter molecule moves faster.
   B) Both move with the same speed. D) The heavier molecule moves faster.
2. Gas at a pressure P is contained in a vessel. If the masses of all the molecules are doubled and their speeds halved, then what will be the resulting pressure?
   A) 2P B) 1/3P C) ½ P D) 3P
3. An ideal gas is at a temperature of 300K. If we wish to double the root mean square (rms) speed of the molecules of the gas, to what value must we rise its temperature?
   A) 450K B) 600K C) 800K D) 1200K

## Brownian Motion And Diffusion

Brownian motion is a random movement of particles in a fluid. It was first observed by the Scottish botanist Robert Brown. The particle in the fluid (liquid or gas) was being constantly bombarded from all sides by molecules of the fluid. If the particle is very small, because the impacts are seemingly random on occasion it gets more hits on one side than the other. This gives rise to a net force and causes the particle to accelerate in the direction of this net force. These small movements are what make up Brownian motion.

Mean free path:- is the average distance covered by the particle between successive collisions. In a gas, the lower the pressure of the gas, or the lower the temperature, the greater is the mean free path. To determine the mean free path consider a molecule with a diameter d travelling with a velocity v. In a time t our molecule sweeps out a cylinder of cross-sectional area $A= \pi d^2$ and length *vt*.




$$\text{Mean free path} = \frac{\text{Distance moved by a molecule in a time t}}{\text{Number of molecules inside the volume swept by the molecule}}$$

$$\ell = \frac{vt}{\pi d^2 n v t} \text{ Or } \quad \ell = \frac{1}{\pi d^2 n}$$ where n is number of molecules per unit volume

In the above expression for the mean free path, it is assumed that all the molecules are at rest. When moving molecules are considered, the result becomes

$$\ell = \frac{1}{\sqrt{2}\pi n d^2}$$

Example

1. How many molecules are there in each $cm^3$ that have mean free path of 2m? (Diameter of the molecule= $3\times10^{-8}$m). **Ans**. n= $1.25\times10^{8}$molecules/$cm^3$
2. Find the m.f.p of molecules under S.T.P if radius of the molecule is $3\times10^{-10}$m. At S.T.P $N_A$= $6.02\times10^{23}$molecules occupy a volume of $22.4m^3$. **Ans**. $\ell=2.33\times10^{-5}$m

Exercise

1. At what pressure will a mean free path be 50cm for spherical molecules of radius $3\times10^{-10}$m at a temperature of $27^0$C? **Ans**. P= $5.18\times10^{-3}$Pa
2. Find the mean free path and average time between collision at S.T.P if $v_{rms}$= 490m/s and r= $2\times10^{-10}$m. **Ans**. $\ell=5.24\times10^{-5}$m, $\Delta t= 1.1\times10^{-7}$sec.
3. What is the mean free path of a gas molecule with r= $2.5\times10^{-10}$mm in an ideal gas at $427^0$C when the pressure is $76\times10^{-6}$mm Hg? **Ans**. $\ell$= 0.0746m

## Second Law Of Thermodynamics

The second law of thermodynamics states:-

*i*) Heat flows from a hotter to a colder object; not vice versa.

*ii*) The complete conversion of energy from a hot reservoir into work is not possible.

*iii*) No process is possible in which there is an overall decrease in entropy of the universe.

Heat sink:- is a body which absorbs heat from other body which is in thermal contact.

Heat engine:- is a device that converts heat ( thermal energy) into other useful energies such as mechanical energy.

Heat engines are classified into two groups

1. External combustion heat engine:- is an engine in which *the burning of fuel takes place outside the engine.*
   Eg. Steam engine
2. Internal combustion heat engine:- is an engine in which *the burning of fuel takes place inside the engine.*
   Eg. Petrol engine, diesel engine

Working substance of heat engines:- is a substance that flows in a cyclic process.

- The working substance of
  * a steam engine is *water* (*steam*)
  *a heat engine is *compressed air*

As the working substance is carried through a cyclic process, the engine

*i*) absorbs (takes in ) heat, $Q_h$, from a high-temperature, $T_h$, energy reservoir

*ii*) work is done by the engine

*iii*) expels (rejects) heat, $Q_c$, to a cold temperature reservoir (the surrounding) at temperature, $T_c$,

The work done by a heat engine is given by

$$W= Q_h - Q_c$$

Efficiency of heat engine is

$$Efficiency = \frac{The\ net\ work\ done}{The\ heat\ absorbed during\ a\ cycle}$$

$$e=\frac{W}{Q_h} \qquad e = \frac{Q_h - Q_C}{Q_h} \qquad \text{Or} \qquad e = 1 - \frac{Q_C}{Q_h}$$

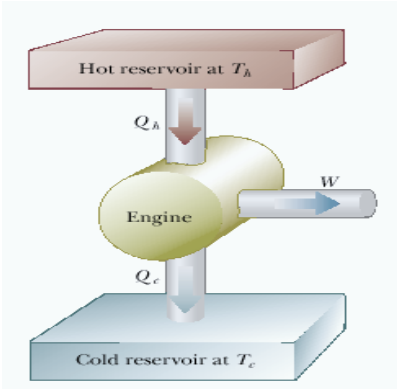
We see that efficiency of a heat engine increases as $Q_C$ decreases relative to $Q_H$.

The maximum theoretical efficiency is

$$e = \frac{T_h - T_C}{T_h} \qquad \text{Or} \qquad e = 1 - \frac{T_C}{T_h}$$

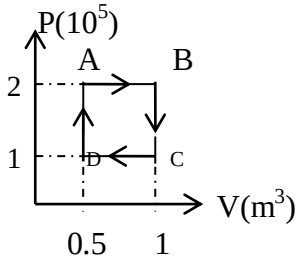
As you see from the above equation, a heat engine will have a 100% efficiency (e=1) only if $Q_C = 0$, i.e., if no heat is expelled to the cold reservoir. That means the engine converts all the thermal energy that it absorbs into useful work, which is impossible.

*A schematic diagram of heat engine*




Example

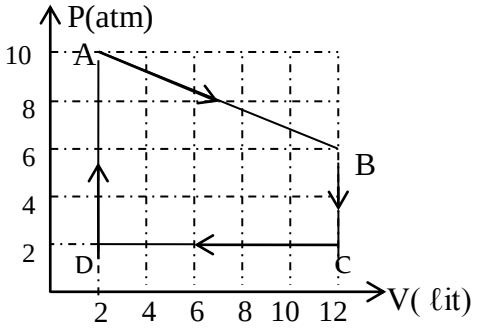
1. A certain heat engine has an efficiency of 25%. For each 1000J of heat energy it takes in
   a)how much output work does it do? **Ans**. W= 250J,b) how much does it exhaust? **Ans**. $Q_C$= 750J
2. An engine takes 2000J of heat from a hot reservoir at $527^0$C and discards some heat to cold reservoir at $127^0$C.
   a) What is the maximum theoretical efficiency? **Ans**. $e_{max}$= 50% or $e_{max}$= 0.5
   b) How much work does the engine do? **Ans**. W= 1000J
3. For the thermodynamic cycle shown below, what is the work done in portion
   a) AB of the cycle? **Ans**. $W_{AB} = 10^5$J
   b) BC of the cycle? **Ans**. $W_{BC}$ =0J
   c) CD of the cycle? **Ans**. $W_{CD} = -5\times10^4$J
   d) DA of the cycle? **Ans**. $W_{DA}$= 0J




4. Calculate the net work done by the engine in question 3 above. **Ans**. $W_{net}$ = 50000J

Exercise

1. An engine takes in 10,000J of heat and delivers 2000J of mechanical work.
   a) What is the thermal efficiency? **Ans**. e= 20% or e= 0.2
   b) How much heat is delivered during each cycle? **Ans**. $Q_c$= 8000J
2. What is the maximum theoretical efficiency of a heat engine that operates between two temperatures $227^0$C and $27^0$C? **Ans**. e= 40%
3. Consider the thermodynamic cycle shown below. What is the work done in portion
   a) AB of the cycle? **Ans**.$W_{AB}$= 8000J
   b) BC of the cycle? **Ans**. $W_{BC}$ =0J
   c) CD of the cycle? **Ans**. $W_{CD}$= – 2000J
   d) DA of the cycle? **Ans**. $W_{DA}$= 0J




4. What is the net work done (net work output ) by the engine in question 3 above? **Ans**. $W_{net}$ = 6000J

5. The highest theoretical efficiency of a certain engine is 30%. If this engine uses the atmosphere, which has a temperature of 300 K, as its cold reservoir, what is the temperature of its hot reservoir? **Ans**. $T_H$= 430K
6. The heat absorbed by an engine is five times the work it performs. What is its thermal efficiency? **Ans**. e= 20%

## *Questions from national exam*

1. The second law of thermodynamics does NOT imply that:
   A) there is no process in which there is an overall decrease in the entropy of the universe.
   B) the complete conversion of energy from a hot source into work is not possible.
   C) heat flows from colder body to hotter body as in the refrigerator without work done on the system.
   D) perfectly reversible processes are impossible
2. Which of the following combinations of properties would be most desirable for a heat sink in a machine?
   A) High specific heat and low conductivity. C) High specific heat and high conductivity.
   B) Low specific heat and high conductivity. D) Low specific heat and low conductivity.
3. A heat engine is being designed to have a Carnot efficiency of 65.0% when operating between two energy reservoirs. If the temperature of the cold reservoir is at $20.0^0$C, what must be the temperature of the hot reservoir?
   A) $57^0$C B) $310^0$C C**)** $564^0$C D) $807^0$C
4. A device for transforming heat energy to mechanical energy is:
   A) transformer C) generator
   B) refrigerator D) engine
5. A certain heat engine draws 500 calories from a water bath $27^0$C and rejects 400 calories to a cold reservoir. What is the efficiency of this engine?
   A) 80% B) 75% C) 25% D**)** 20%

## The Internal Combustion Engine

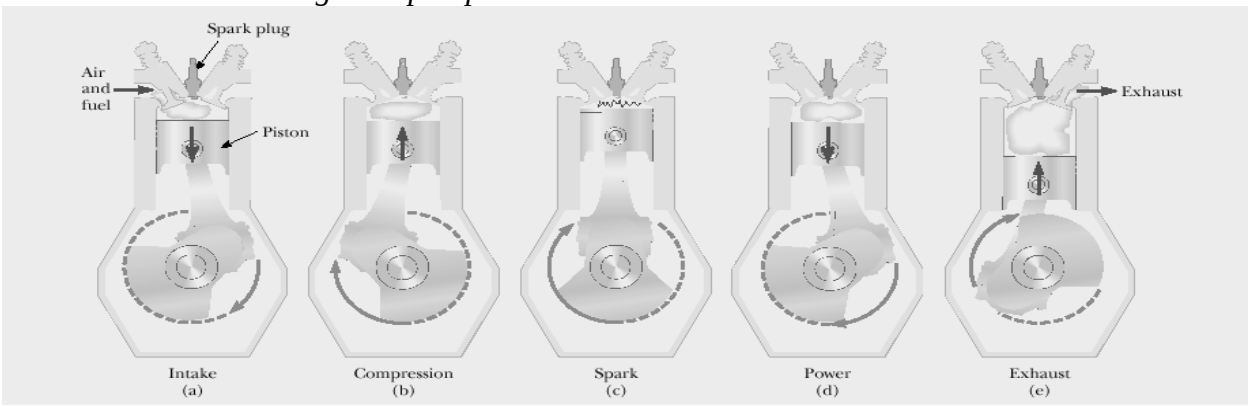
A typical car engine can be represented by a piston moving up and down in a cylinder causing a shaft to rotate. The complete cycle of events takes four strokes of the piston as follows.

*i*) The intake stroke, a ⟶ b:- *The inlet valve opens and the mixture of air and petrol is drawn into the cylinder at constant pressure as the piston* moves *down ( volume of the gas increases*).

*ii*) The compression stroke, b ⟶ c:- *The valve is closed and the piston moves up compressing the mixture adiabatically so that the temperature and pressure increase. The fuel-air mixture is ignited by the spark from the spark plug. Combustion occurs very quickly and as a result the process can be considered to be isochoric,* c ⟶ d:- *There is a significant amount of heat* ($Q_h$) *released. This resulted in an increase in the temperature and pressure of the gas inside the piston.*

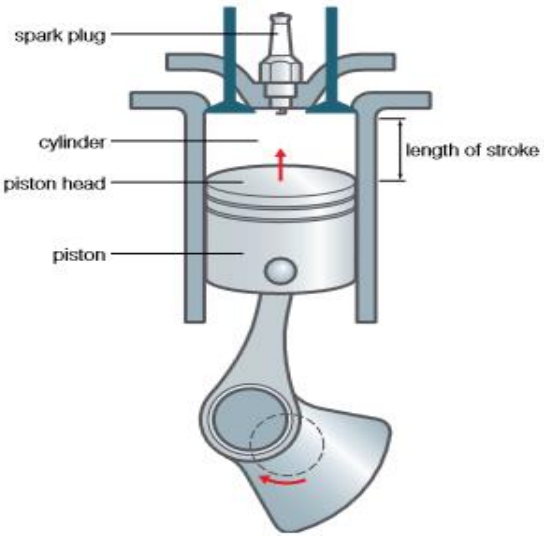
*iii)* The power stroke, d ⟶ e:- *The hot high pressure gas expands adiabatically pushing the piston down.*

*iv)* The exhaust stroke, e ⟶ a:- *The exhaust valve opens and the piston pushes out the exhaust gas* ( $Q_C$). *The temperature decreases causing a drop in pressure.*

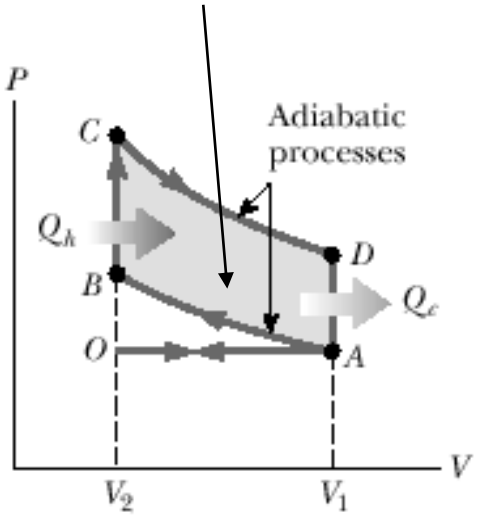


## The Otto Cycle

The indicator diagram below shows an Otto cycle in simplified form, what happens in a cylinder of a four stroke petrol engine

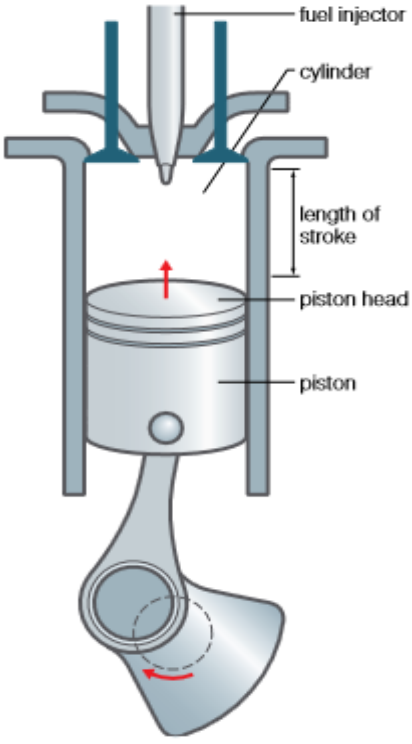



Area= net work done by the engine

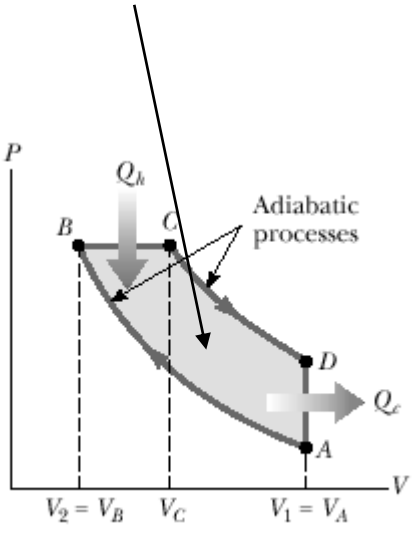



## Diesel engines

- have no spark plug
- have long pistons compared to the petrol one. As a result they use high compression ratios $V_1/V_2$ and operates at higher efficiencies than Otto engines
- fuel is injected after compression
- heat is added at constant pressure




Area = net work done by the engine

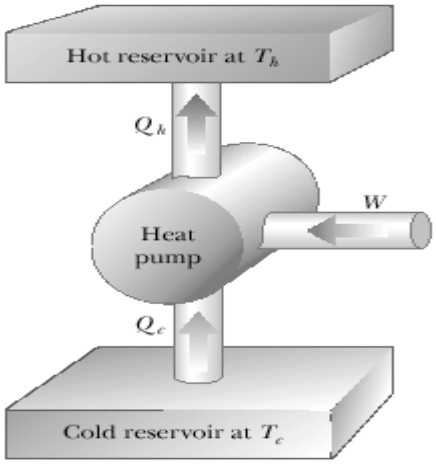


Questions

1. Fuel is injected after compression in _____engine.
2. Heat is added at constant a) volume in _____engine. b) Pressure in _____engine.
3. A type of engine that extracts heat $Q_c$ to cold reservoir at constant volume is_____ engine.

## The refrigerator

According to the second law of thermodynamics *heat does not by itself flow from cold to hot body*. However, if outside work is done, it is possible to make heat flow from cold to hot body.




Heat $\mathbf{Q_c}$ is extracted from the low-temperature reservoir at temperature $\mathbf{T_c}$ and heat $\mathbf{Q_h}$ is discarded to high temperature reservoir at $\mathbf{T_h}$. The system pumps heat from the low-temperature (colder) chamber to the outside. The coefficient of performance **η** of a refrigerator is given by

$$\eta = \frac{Extracted\,heat}{Input\,work}$$

$$= \frac{Q_C}{W_{in}} \qquad \eta = \frac{Q_C}{Q_h - Q_C} \qquad \text{Or} \qquad \eta = \frac{T_C}{T_h - T_C}$$

The larger this ratio, the better the performance, since more energy is being removed for a given amount of work.

* *A **heat engine** has a net **output of mechanical work**; a **refrigerator** has a net **output of heat**.*

*A working substance in a refrigerator is refrigerant fluid.

Example

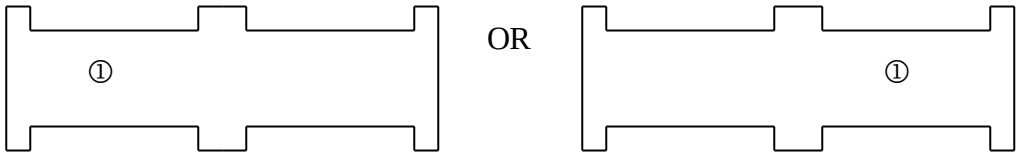
1. A refrigerator exhausts 250J of heat to a room while the motor provides 80J of work per cycle
   a) How much heat is extracted from the interior of the refrigerator? **Ans**. $Q_c$= 170J
   b) What is the coefficient of performance of the refrigerator? **Ans**. η= 2.125
2. A refrigerator extracts $2\times10^8$J of heat from the interior of the refrigerator each hour. If it operates with a coefficient of performance of 4, determine for each hour of operation
   a) the work done on the refrigerator. **Ans**. W= $5\times10^7$J, b) the heat exhausted to the outside. **Ans**. $Q_h$= $2.5\times10^8$J
3. A refrigerator extracts 2700J of heat from a cold chamber at a temperature of 270K. If the outside temperature is 300K, find
   a) its coefficient of performance. **Ans**. η= 9, b) $Q_h$. **Ans**. $Q_h$= 3000J, c) work done on the refrigerator. **Ans**. W= 300J
4. An ordinary refrigerator is turned on and its door is left open in a thermally insulated kitchen. What will happen to the temperature of the room?
   A) Increases according to the first law of thermodynamics.
   B) Decreases according to the first law of thermodynamics.
   C) Remains constant according to the first law of thermodynamics.
   D) Remains constant according to the second law of thermodynamics

# Entropy

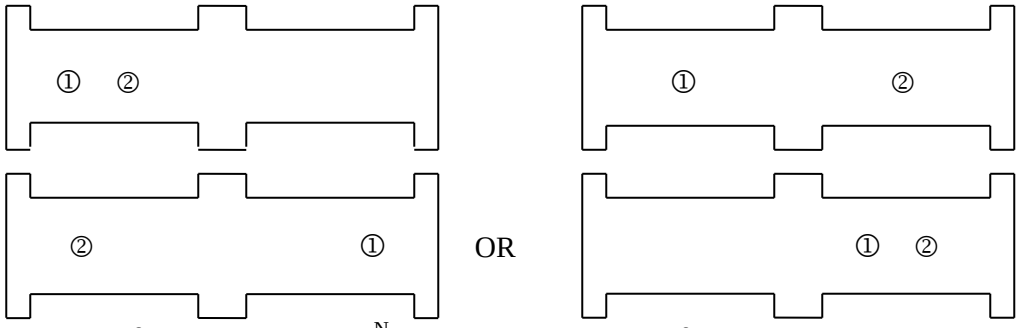
Entropy:- is the measure of the amount of disorder in a system. The measure of disorder is equal to the number of ways that the system may be arranged.

After the cover slide is removed

For *one* molecule, *there are two ways of arrangements*. Number of arrangements = $2^1 = 2$
the molecule is either in the left-hand or in the right-hand cylinder.

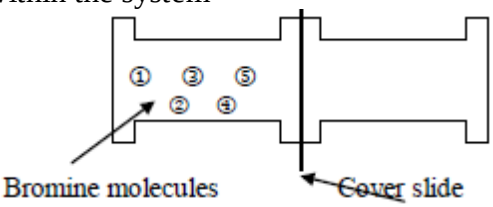



For *two* molecules, *there are four ways of arrangements*. Number of arrangements = $2^2 = 4$




In general, *number of arrangements* = $2^N$. Where N = number of molecules.

For 5 molecules, there are 32 possible arrangements within the system .




*Before the cover slide was removed, there was only one possible arrangement for the five particles; they were all in the left-hand cylinder. The entropy of the system was small.*

After the cover slide was removed, the amount of disorder in the system, and hence its entropy, increases as there are 32 possible arrangements for the particles.

*If the number of possible arrangements (amount of disorder) in a system is* $W = 2^N$.

The entropy of the system (S) is

$S = k \ell n W$ Where $k = 1.38 \times 10^{-23}$ J/K Boltzmann's constant

When heating occurs at a constant temperature, the change in entropy $\Delta S$ is given by

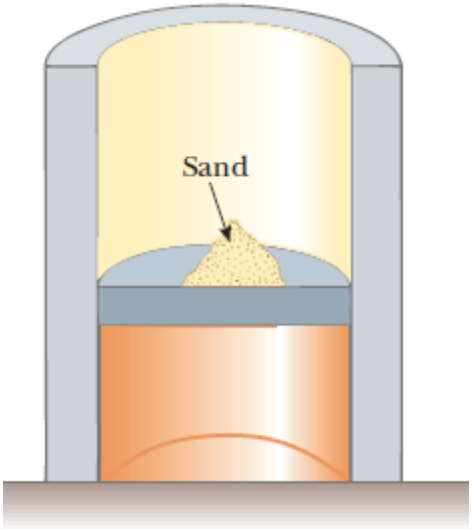
$$\Delta S = \frac{\Delta Q}{T}$$ Where T is in Kelvin

The entropy of a system never decreases. It **increases** for an **irreversible process** and **remains constant** for a **reversible process**.

Because entropy is a measure of disorder, an alternative way of stating this is **the entropy of the Universe increases in all real processes.** The change in entropy during a process depends only on the end points and therefor is independent of the actual path followed. Consequently, the entropy change for an irreversible process can be determined by calculating the entropy change for a reversible process that connects the same initial and final states.

In a reversible process, the system undergoing the process can be returned to its initial conditions along the same path on a *PV* diagram, and every point along this path is an equilibrium state. A process that does not satisfy these requirements is **irreversible**.

Most natural processes are known to be irreversible; the reversible process is an idealization. Although real processes are always irreversible, some are *almost* reversible. If a real process occurs so slowly that the system is virtually always in equilibrium, the process can be considered reversible. Imagine compressing a gas very slowly by dropping grains of sand onto a frictionless piston, as in figure below. The temperature can be kept constant by placing the gas in thermal contact with an energy reservoir. The pressure, volume, and temperature of the gas are well defined during this isothermal compression. Each added grain of sand represents a change to a new equilibrium state. The process can be reversed by slowly removing grains of sand from the piston.




****Reversible*:- *a process that can be reversed by means of an infinitesimal change in a property of the system without a transfer of energy.***

The second law of thermodynamics states:- " ***No process is possible in which there is an overall decrease in the entropy of the universe."***

Example

1. Workout the entropy of a bromine gas after the cover slide is removed;
   a) for 1molecule. **Ans**. $S= 9.6\times10^{-24}$J/K.
   b) for 2 molecules. **Ans**. $S= 1.9\times10^{-23}$J/K
   c) for 3 molecules. **Ans**. $S= 2.9\times10^{-23}$J/K
   d) for 4 molecules. **Ans**. $S= 3.8\times10^{-23}$J/K
   e) for 5 molecules. **Ans**. $S= 4.8\times10^{-23}$J/K
2. A gas is allowed to expand adiabatically and reversibly. What is the change in entropy?

Exercise

1. One kilogram of ice at $0^0$C is melted and converted to water at $0^0$C. Calculate the change in entropy. ($L_f = 3.34\times10^5$J/kg)**Ans**. $\Delta S= 1223$J/K
2. What is the change in entropy of 5g of water at $100^0$C as it is converted to steam at $100^0$C? ($L_v= 2.256\times10^6$J/Kg) **Ans**. $\Delta Q = 11280$J, $\Delta S= 30.24$J/K

## *Questions from national exam*

1. In a reversible thermodynamic process, the system
   A) is always close to equilibrium states.
   B) might never be close to any equilibrium state.
   C) is close to equilibrium states only at the beginning and end.
   D) is close to equilibrium states throughout, except at the beginning and end.
2. The change in entropy is zero for:
   A) reversible isobaric processes.
   B) reversible adiabatic processes.
   C) reversible isothermal processes.
   D) reversible processes during which no work is done.
3. Which one of the following statements is NOT correct?
   A) The entropy of the Universe increases in all natural processes.
   B) No heat engines operating in a cycle can absorb energy from a reservoir and use it entirely to do work.
   C) When a system undergoes a change in state, the change in its internal energy is the difference between the energy transferred to it by heat and the work done on it.
   D) The entropy of an isolated system reaches its maximum value when the system is in equilibrium state.
4. Which of the following statements is correct?
   A) Irreversible process is a process that can be reversed through finite change in the system.
   B) Complete conversion of energy from a hot source into work is possible.
   C) There is a process in which there is an overall decrease in entropy.
   D) Entropy is a measure of the amount of disorder.