## Molar heat capacity of gases :—

Heat capacity (c) of a substance is defined as the amount of heat required to raise the temp. of the substance by one degree. Heat capacity per gram of a substance is called specific heat and per mole is called molar heat capacity.

Thus,        Molar heat capacity = molar mass × specific heat

For gases, there are two heat capacities at const. vol. and at const. Pr. So, $C_V = M \times c_v$ and $C_p = M \times c_p$, where $C_V$ and $C_p$ are the molar heat capacities at const. vol. and at const. Pr., respectively. $c_v$ and $c_p$ are their specific heats.
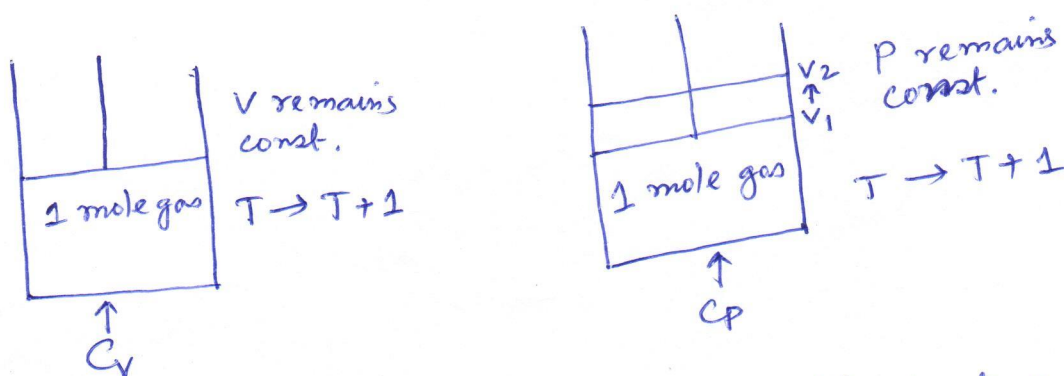


From the above two schematic descriptions, it is clear that $C_p > C_V$, since for $C_p$, some mechanical work is required as additional energy to absorb for lifting the piston from $V_1$ to $V_2$.

Thus, $C_p - C_V$ = Mechanical work
$$= P\,dV = P(V_2 - V_1) = PV_2 - PV_1 = R(T+1) - RT$$
$$= R \qquad PV = RT$$

Thus, $C_p - C_V = R$. This is valid for ideal gas only as $PV = RT$ is taken for 1 mole gas.

Now let us find the expression for $C_V$ from the stand-point of the kinetic theory of gas.

$C_V$ = Energy required to increase translational kinetic energy + energy required to increase intramolecular energy of 1 mole gas for 1 degree rise in temperature.

Increase of translational KE of 1 mole gas for $1°$ rise in temp.

$$= \frac{3}{2} R(T+1) - \frac{3}{2} RT = \frac{3}{2} R$$

Let the intramolecular energy increase for the gas for $1°$ rise in temp $= x$. Then,

$$C_V = \frac{3}{2} R + x$$

$\frac{3}{2} R$ = Translational contribution

$x$ = (Rotational + Vibrational) contribution

The value of $x$ is calculated from the law of equipartition of energy and this will be discussed later.

Thus, $C_p = \frac{5}{2} R + x$

The molar heat capacity ration (Poisson ratio),

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2} R + x}{\frac{3}{2} R + x} = \frac{5 + x}{3 + x}$$

when expressed in calorie unit. and $R = 2$ cal $mol^{-1} K^{-1}$

For monatomic gas, $x = 0$, $\gamma = \frac{5}{3} = 1.66$

For diatomic gas, $x = R = 2$ cal $mol^{-1} K^{-1}$; $\gamma = \frac{7}{5} = 1.4$

For polyatomic gas, $x = \frac{3}{2} R = 3$ cal $mol^{-1} K^{-1}$; $\gamma = \frac{4}{3} = 1.33$

For a gas, $\gamma$ can be determined from the measurement of velocity ($v$) of sound passing through the gas using the relation, $v = \sqrt{\frac{\gamma RT}{M}}$. The value of $\gamma$ thus provides the atomicity (molecular complexity) of the gas.

Internal eng. is entirely kinetic. For monatomic gases (He, Ne, etc) there is only translational K.E (as no rotation or vibration) is possible for monatomic molecule

$x$: cannot be derived from kinetic gas equation.
Thus, Kinetic theory fails to theoretically calculate $C_p$ & $C_V$ values for diatomic and polyatomic gases.

## Maxwell's speed distribution :-

James clerk Maxwell (1859) formulated speed distribution of particles in idealized gases where the particles move freely inside a stationary container without interacting with one another. On the basis of probabilistic idea, Maxwell and later Boltzmann formulated the distribution law. This distribution describes how the different speeds are distributed among various group of molecules.

$F(c) \rightarrow$ Maxwell speed distribution function

where $F(c) = \frac{1}{n} \frac{dn_c}{dc}$

$n = $ no of molecules per unit volume

$dn_c = $ " " " within the speed range $c$ to $(c+dc)$

$$F(c) = \frac{1}{n} \cdot \frac{dn_c}{dc} = \left(\frac{m}{2\pi RT}\right)^{1/2} e^{-\frac{mc^2}{2RT}} \qquad (1-D)$$
one Dimentional velocity distribution

$$F(c) = \frac{1}{n} \cdot \frac{dn_c}{dc} = 2\pi \left(\frac{m}{2\pi kT}\right) \cdot c \cdot e^{-\frac{mc^2}{2RT}} \qquad (2-D)$$

$$F(c) = \frac{1}{n} \cdot \frac{dn_c}{dc} = 4\pi \left(\frac{m}{2\pi RT}\right)^{3/2} \cdot c^2 \cdot e^{-\frac{mc^2}{2RT}} \qquad (3-D)$$

$m = $ Molecular mass of the gas ; $T = $ Temp. in absolute scale.

It is assumed that the gas molecules remain in complete random and the probability of a molecule to have a definite speed within small range is always finite.

we can also write, $F(c) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \cdot c^2 \cdot e^{-\frac{Mc^2}{2RT}}$

Thus, $F(c)$ depends on the nature of the gas which is characterized by molar mass (M) and the temp (T). Thus, $F(c)$ depends on $\frac{M}{T}$ of the gas. Thus, $F(c)$ of $O_2$ gas molecules at 300 K is same as

as that of $SO_2$ gas molecules at 600 K as $\frac{M}{T}$ value is same for both the gases at these temperatures. It means that fraction of $O_2$ molecules at 300 K have the same velocity with that of $SO_2$ gas at 600 K. Similarly, $F(c)$ of $N_2$ gas and CO gas is same at any temp. as both the gases have same molar mass.

### Salient features of Maxwell's distribution curve:-

It is possible to calculate $F(c)$ of a particular gas at a given temp. with different speeds ranging from small value to high value. The calculated values can be put in a table and then it can be projected in a Figure, $F(c)$ vs. $c$.

For $O_2$ gas 300 K

| Speed | function |
|-------|----------|
| 0 | 0 |
| $c_1$ | $F(c_1)$ |
| $c_2$ | $F(c_2)$ |
| $c_3$ | $F(c_3)$ |
| $c_4$ | $F(c_4)$ |
| ⋮ | ⋮ |
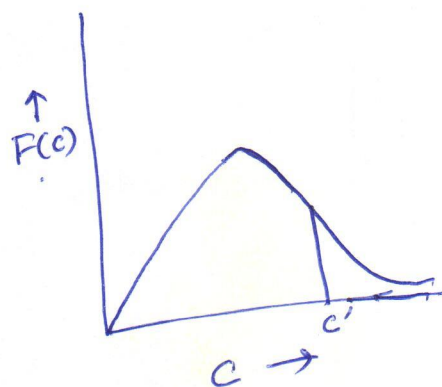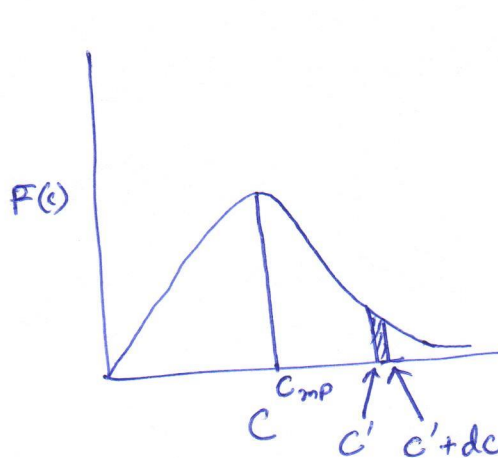


Various conclusions can be drawn from the $F(c)$ vs. $c$ curve.

① The curve initially rises in parabolic form with increasing speed, reaches a maxima and then falls off exponentially.

② The ~~fraction~~ total no. of molecules within a certain speed range $c'$ to $(c'+dc)$ is given by the area of the shaded region: $F(c') \times dc$. Total area of the curve is unity, i.e., fraction of molecules that have speed 0 to ∞ is one.

③ Maximum fraction of the molecules have a common speed, it is called most probable speed ($C_{mp}$).

④ $F(c)$ contains two factors: one is exponential term, $e^{-\frac{mc^2}{2RT}}$ and the other is non-exponential term, $c^2$. Thus, with increase of $c$, the exponential term decreases the value of $F(c)$ while the non-exponential term increases the value of $F(c)$. So, the net effect on $F(c)$ depends on the relative magnitude of these two factors. At low ~~conc~~ $c$, the non-exponential term dominates while at high $c$, exponential term dominates. Thus, the value of $F(c)$ starts from zero at $c = 0$, increases, then attains maximum and finally decreases toward asymptotic value with increase of $c$. The value of $F(c)$ again becomes zero at $c \to \infty$

⑤ when $c = 0$, $F(c) = 0$. It means that there is no molecule that have zero speed i.e. no molecule is at rest at any temp., all molecules are moving in the gaseous phase.

## Effect of temp. on the distribution :-

① $F(c)$ contains two factors which are dependent on $T$, one is exponential term, $e^{-mc^2/2RT}$ and the other is non-exponential term, $\left(m/2\pi RT\right)^{3/2}$. So distribution curve varies when the temp. of the gas is increased.



$T_3 > T_2 > T_1$

$C_{mp}(T_1)$         $C_{mp}(T_3)$
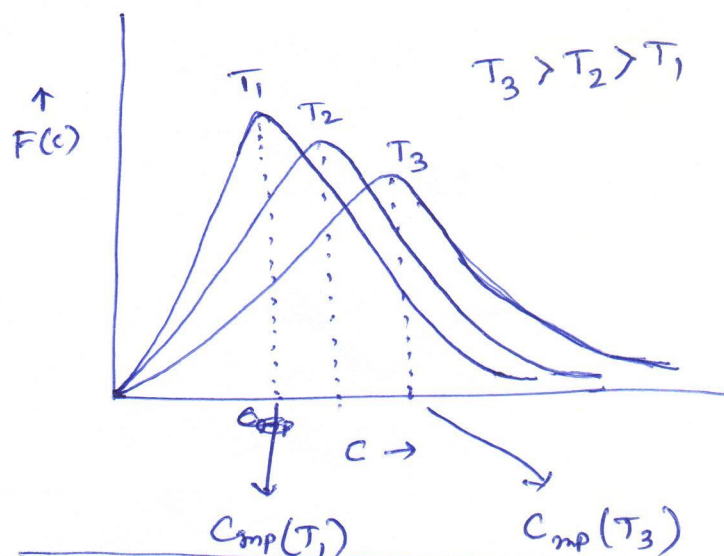
② The most-probable speed is increased with rise in temp. However the fraction of molecules having most-probable speed is decreased.

Thus, if $T_2 > T_1$, then ~~$\frac{C_{mp}}{C_{mp}(T_2)} > C$~~

$C_{mp}(T_2) > C_{mp}(T_1)$, but $F(C_{mp})$ at $T_2 < F(C_{mp})$ at $T_1$

③ The fraction of molecules having speed close to $C_{mp}$ is also large as the curve is flat at higher $T$.

④ when $T \uparrow$, the curve becomes more and more flat. when $T \to \infty$, the curve lies on the $C$-axis indicating that the speed distribution is totally uniform. All the molecules have same speed and in fact distribution is lost.

⑤ If $T \downarrow$, the curve becomes narrow. when $T \to 0K$, the curve lies on the $F(c)$-axis. All the molecules have speed zero and so again distribution is lost.

⑥ The total area in both the cases of $T_1$ and $T_2$ is Same and it is unity.

## Effect of molar mass on distribution :-

The molar mass $(M)$ and temp $(T)$ remain in the expression of $F(c)$ as $\left(\frac{M}{T}\right)$. So, the effect of $M$ is just the opposite to that of $T$.

The curve for the gas of lower molar mass (such as He) is wider than the gas of heavier molar mass (such as Argon).
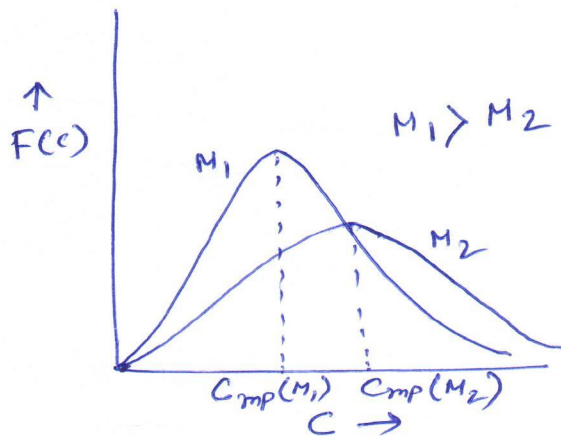


## Kinetic energy distribution from Maxwell's speed distribution :-

$$\frac{1}{n} \frac{dn_c}{dc} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \cdot c^2 \cdot e^{-mc^2/2kT}$$

Kinetic energy, $\varepsilon = \frac{1}{2} mc^2 \Rightarrow d\varepsilon = \frac{1}{2} \cdot 2mc \cdot dc$

$$\Rightarrow dc = \frac{d\varepsilon}{mc} = \frac{d\varepsilon}{m\sqrt{\frac{2\varepsilon}{m}}} = \frac{d\varepsilon}{(2m\varepsilon)^{1/2}}$$
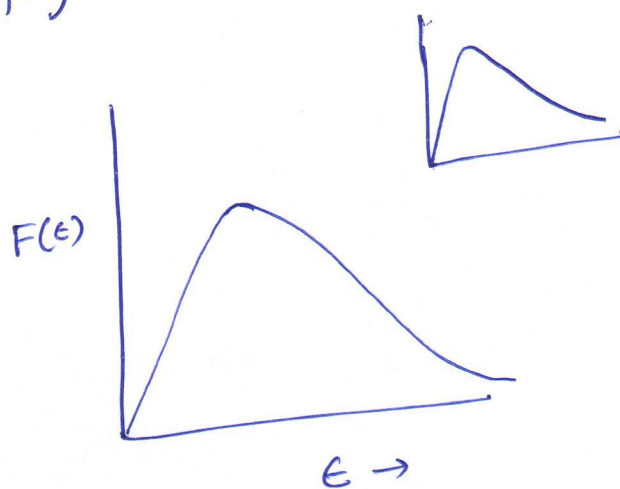
Substituting $dc$ and $c^2$ in the equ$^n$:

$$\frac{1}{n} \frac{\frac{dn_E}{dE}}{(2mc)^{1/2}} = 4\pi \left(\frac{m}{2\pi RT}\right)^{3/2} \cdot \frac{2E}{m} \cdot e^{-m \cdot \frac{2E}{m}/2RT}$$

$$\Rightarrow \frac{1}{n} \frac{dn_E}{dE} = 4\pi \left(\frac{m}{2\pi RT}\right)^{3/2} \cdot (2mE)^{-1/2} \cdot \left(\frac{2E}{m}\right) e^{-E/RT}$$

$$\Rightarrow F(E) = \frac{1}{n} \cdot \frac{dn_E}{dE} = 2\pi \left(\frac{1}{\pi RT}\right)^{3/2} \cdot E^{1/2} e^{-E/RT}$$

note, $F(E)$ does not contain the molecular mass of the gas.

This means that KE distribution only depends on $T$ but does not depend on the nature of the gas.

$F(E)$

$E \rightarrow$

Since, $E$ is fraction and small, so $\sqrt{E} > E$ and non-exponential term ($\sqrt{E}$) dominates more, so $\sqrt{E} > E$ and non-exponential term ($\sqrt{E}$) dominates more, so the plot of $F(E)$ vs. $E$ gives the KE distribution curve that rise more steeply but falls more slowly than the speed distribution curve.