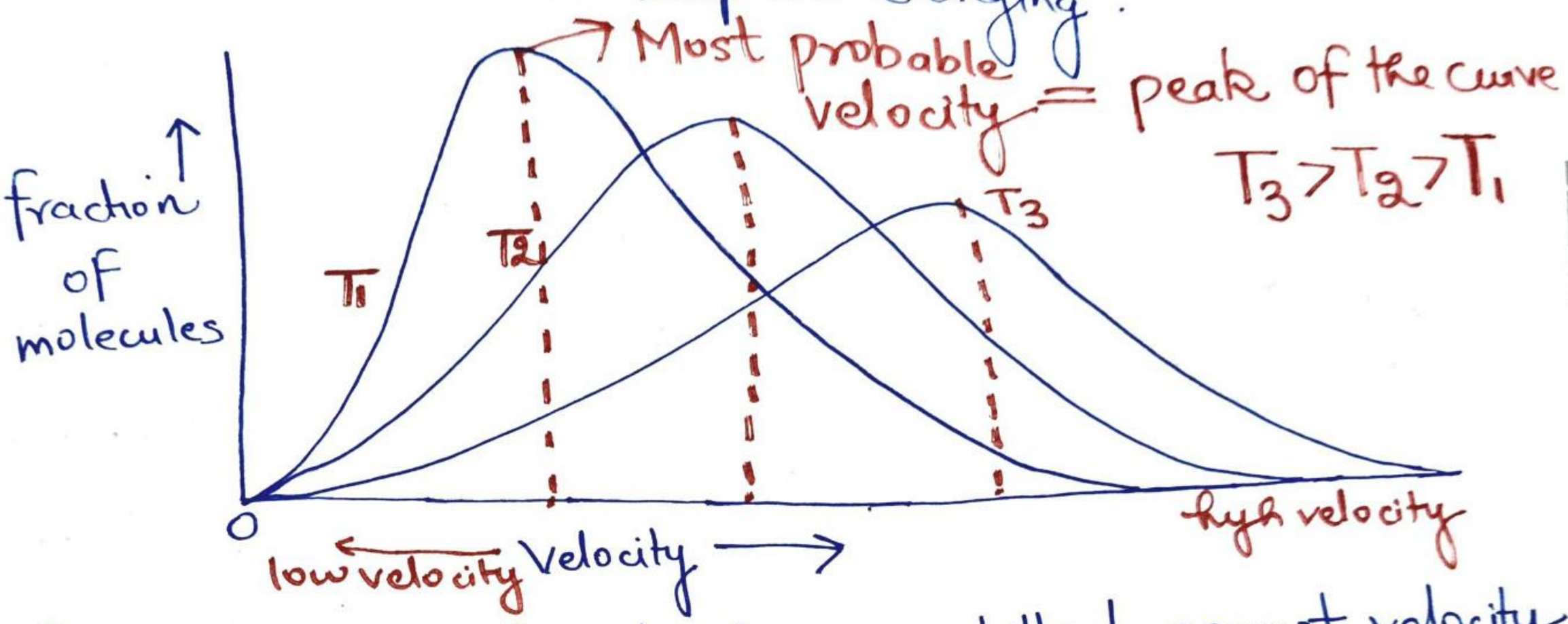
Maxwell Boltzmann distribution laws of molecular velocities

As a result of random collisions of gaseous molecules, the molecular velocities keep on changing.



Here fraction of molecules are plotted against velocity (The plot is used to determine how many molecules are moving between different velocities (b/w velocity c and c+dc))

Fraction of molecules having velocities greater than zero increases with an ↑se in velocity, reaches a maximum and then falls off towards zero ~~against~~ again at higher velocities (see plot)

The important features of the above drawn curves :→

(i) The fraction of molecules with very low OR very high velocities is very small.

(2) There is a certain velocity for which the fraction of molecules is maximum. This is called the most probable velocity.

The most probable velocity of a gas is the velocity possessed by maximum no. of molecules of the gas at a given temperature. It corresponds to the peak of the curve. Its value at a given temperature depends upon the volume of gas.

Effect of temp on distribution of molecular Velocities :-

The most probable velocity increases with rise in temperature. The entire distribution curve shifts to the right with rise in temperature. The rise in temperature ∴, ↑ses the fraction of molecules having high velocities considerably.

Fraction of molecules can be expressed as

$$\frac{dN}{N} = 4\pi \left(\frac{m}{2\pi KT}\right)^{3/2} c^2 \exp\left(\frac{-mc^2}{2KT}\right) dc \rightarrow (1)$$

$\frac{dN}{N}$ ← total no. of gas molecules

Here presence of factor $\exp\left(\frac{-mc^2}{2KT}\right)$ explain this effect----

The exponent has a -ve sign and the temp T in the denominator. The factor, therefore, ↑es markedly with ↑se in temperature. This factor is known as boltzmann factor

$$\Rightarrow \exp\left(\frac{-mc^2}{2KT}\right)$$

$$\Rightarrow \exp\left(-\frac{\epsilon}{KT}\right) \qquad \epsilon = \frac{1}{2}mc^2 = \text{K.E per molecules of gas.}$$

Greater the temp, the greater is the value of ϵ. Hence there is rapid ↑se of Boltzmann factor with ↑se in temperature.

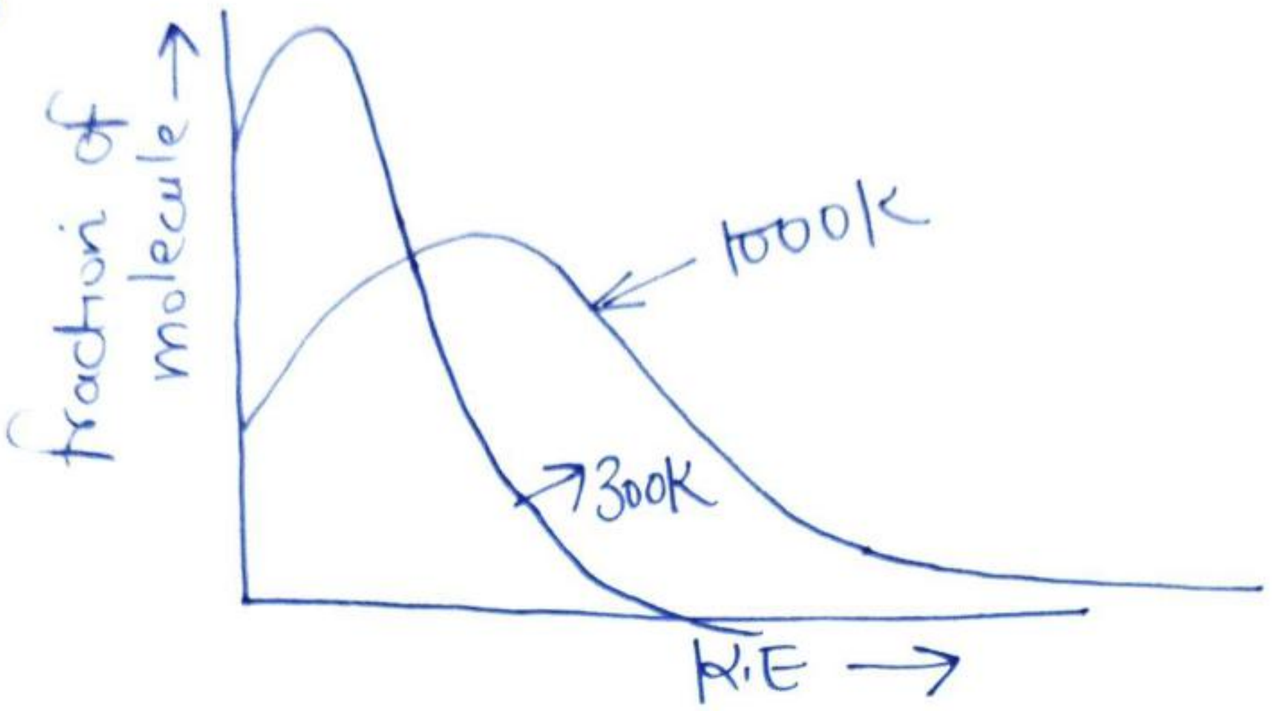
(Some explanation we have seen in theory of reaction rates)

At low temperature, the molecules have less K.E. ∴ the speeds of the molecule is low and the distribution has a small range. As the the temperature of molecules ↑ses (they have high K.E at high temp, ∴ molecules are moving faster), the distribution of molecule flattens out.

causing the Boltzmann plots to spread out.

Maxwell Boltzmann distribution laws of molecular energies :→

It tells how the K·E of molecules are distributed among the various molecules



The Peak of the curve represent the most probable K·E. The most probable K·E ↑ses $\bar{c}$ ↑se in temp.

Different type of molecular velocities

(i) Most probable velocity c_p

The velocity possessed by maximum number of molecules of a gas at a given temp.

(ii) Average velocity $\langle c \rangle$

It is the arithmetic mean of different velocities possessed by molecules of the gas at a given temperature.

$$\langle c \rangle = \frac{c_1 + c_2 + \cdots + c_n}{n}$$

Root mean square velocity ⇒

It is the square root of the mean of the squares of different velocities possessed by molecules of a gas at a given temperature.

$$\langle c^2 \rangle^{1/2} = \left(\frac{c_1^2 + c_2^2 + \cdots c_n^2}{n} \right)^{1/2}$$

With the help of Maxwell eq (1) It is possible to derive the mathematical expression shown below (derivation not in your course)

$$c_p = \left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{2KT}{m}\right)^{1/2}$$

$$\left(\frac{2KT}{N_A M}\right)^{1/2}$$

Boltzmann factor.

gas constant ⇐ $R = \frac{K}{N_A}$

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

$\Rightarrow m = M N_A$

m = mass

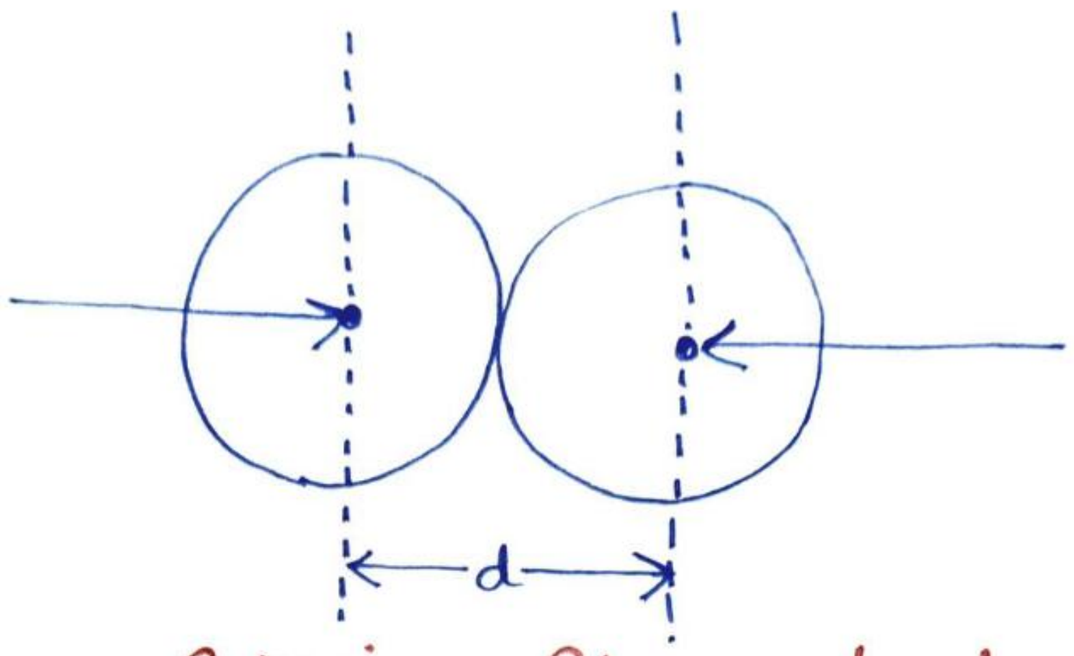
M = molecular weight

$$\langle c \rangle = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8KT}{\pi m}\right)^{1/2}$$

$$\langle c^2 \rangle^{1/2} = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3KT}{m}\right)^{1/2}$$

Collision Parameters

1. Collision diameter

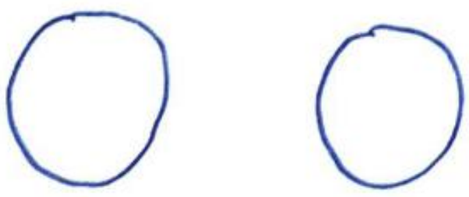


Collision of two molecules.

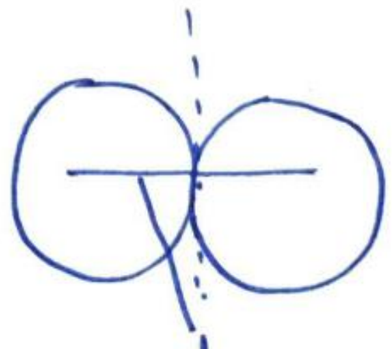
When two molecules approach each other, a point is reached at which the ~~repulsion~~ mutual repulsion between molecules becomes so strong that it causes reversal of the direction of their motion.

The distance b/w centres of the two molecules at the point of their closest approach is known as Collision diameter (d).

A pair of molecule will collide whenever the centres of two molecules come within a distance d of one another.



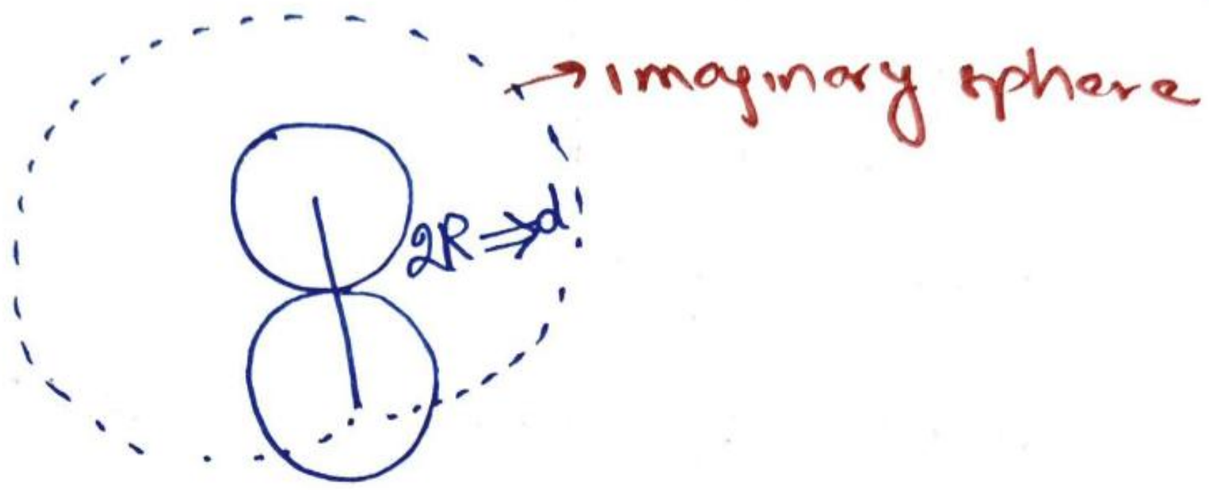
No collision



Collision occurs

2. Collision cross section (σ) of the molecule is the cross sectional area of an imaginary sphere surrounding the molecule into which the centre of another molecule cannot penetrate.

The cross section of the collision is the area of a gread circle which is πd^2 (σ)



3 Mean free path (λ)

⇒ Mean distance travelled by a gas molecule b/w two succesive collisions.

⇒ Average distance a particle travels b/w two collisions

4. Collision frequency (z) ⇒

~~No of collisions~~

Number of molecular collisions occuring per unit time per unit volume of the gas.

The time b/w collision is just the inverse of the collision frequency ie $\frac{1}{Z}$

If the molecule is travelling at a mean speed $< c >$, then (distance = speed x time) mean free path, $< c > \times \frac{1}{Z}$

$$\lambda \Rightarrow \frac{< c >}{Z}$$

Since $Z \propto P$ (collision frequency $\propto$ pressure)

$$\therefore \lambda \propto \frac{1}{P}.$$

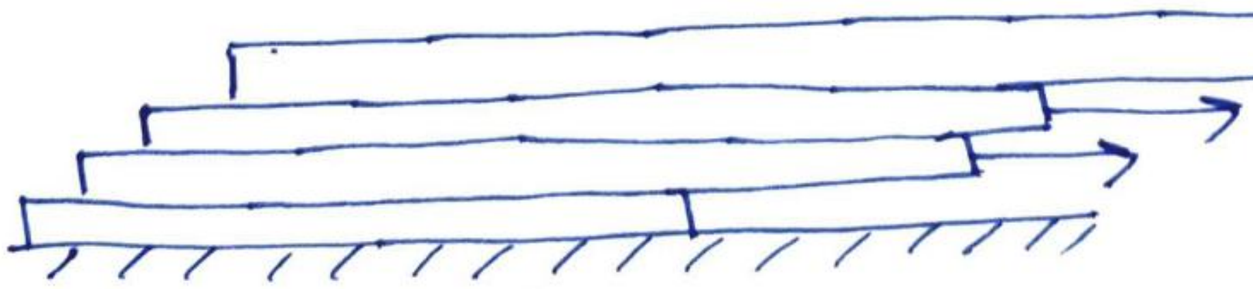
Doubling the pressure will half the mean freepath

Viscosity of gases and effect of temp & pressure on coefficient of viscosity

OR

Transportation of gases / how gas flows

Gases flows in layer (and this flow is called laminar flow) such that each layer moves at a velocity different than the layers adjacent to it.



Adjacent laminar sheets experience friction so that they slide past one another / over one another.

This frictional force is propotional to area b/w sheet: and velocity gradient

$$f \propto \overset{\text{area}}{A} \underbrace{\frac{du}{dr}}_{\text{velocity gradient}}$$

$$f = \eta A \frac{du}{dr}$$

① $\{ f = \eta \frac{du}{dr} \quad (A = 1)$.

↓ weficient of viscosity.

↓ Momentum transferred per unit time $= \frac{1}{3} \int \bar{c} m \lambda \frac{du}{dr}$ ②

OR

Rate of change of momentum

↓ density of gas

Since Rate of change of momentum = force acting

Thus on equation ① & ②

$$\frac{1}{3} \int \bar{c} m \lambda \frac{du}{dr} = \eta \frac{du}{dr}$$

$$\boxed{\eta = \frac{1}{3} \int \bar{c} m \lambda}$$

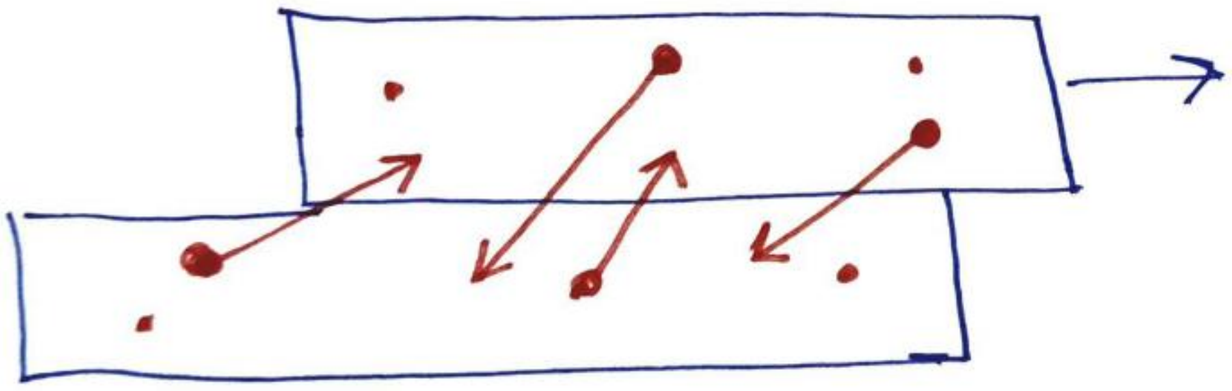
effect of temp and P on η

$$\eta = \frac{1}{3} \lambda \bar{c} \rho_m$$

Since $\lambda \propto \frac{1}{P}$

Viscosity of gas is independent of pressure. At high pressure, more molecules are available to transfer / transport momentum but they carry it less far due to their shorter mean free path ($\lambda \propto \frac{1}{P}$).

[At high P, transfer is great but that effect get cancelled with small mean free path].



In gases, molecular collision transfer momentum b/w layer. As slower molecules collide $\bar{c}$ faster molecules, the slower molecule speed up and the faster molecule slow down.

This effect is observed very often in the skating rinks.

As temp ↑ses, the molecules move faster and more momentum is transferred b/w layers,

thereby ↑sing viscosity

$\bar{c} \propto T^{1/2}$ {average velocity $\left(\frac{8RT}{\pi M}\right)^{1/2}$

Thus $\eta \propto T^{1/2}$ $\left\{\because \eta = \frac{1}{3}\lambda \bar{c} \rho_m\right)$

$\Rightarrow$ Viscosity of ~~gas~~ gas ↑ses $\bar{c}$ ↑se in temperatur

At high temp, molecules have high K.E, moves faster so the trasfer of momentum is great