Introduction

Kinetic molecular theory of gases was first developed by Daniel Bernoulli (1738) and subsequent progress was made by Joule, Clausius, Maxwell and Boltzmann within 1848 to 1898.

Assumptions

This theory consists of the following assumptions:

(1) The gas is composed of very small discrete particles, now called molecules. For a gas, the mass and size of the molecules are same and different for different gases.

(2) The molecules are moving at random in all directions with variety of speeds. Some are very fast while others are slow.

(3) Due to random motion, the molecules are executing collision with the walls of the container (wall-collisions) and also with themselves (intermolecular collisions). These collisions are perfectly elastic and so there occurs no loss of kinetic energy or momentum of the molecules by these collisions. Speed of the molecules remain same due to wall-collisions but may change in intermolecular collisions.

(4) The gas molecules are assumed to be point masses i.e., their size is very small in comparison to the distance they travel.

(5) There exists no intermolecular attractions specially at low pressure i.e., one molecule can exert pressure independent of the influence of the other molecules.

(6) The pressure exerted by a gas is due to the incessant and uniform wall-collisions of the molecules. Higher the frequency of the wall-collisions, greater will be the pressure of the gas. This explains Boyle's law since when volume is reduced, wall-collisions becomes more frequent and the pressure is increased.

(7) Though the molecular speeds are constantly changing due to intermolecular-collisions, average kinetic energy $\left(\bar{\varepsilon}\right)$ of the molecules remains fixed at a given temperature. This explains Charle's law that when temperature is increased, $\bar{\varepsilon}$ is increased, velocities [as $\varepsilon = (1/2)\,mc^2$] are increased, wall-collisions become more frequent and violent, so pressure is increased when volume is kept constant or volume is increased when pressure is kept constant.

Idea of root-mean-square speed $\left(c_{RMS}\right)$

Let in a gas of N molecules, N_1 have speed c_1, N_2 molecules have speed c_2, N_3 molecules have speed c_3 and so on, then

$$\bar{\varepsilon} = \frac{N_1\varepsilon_1 + N_2\varepsilon_2 + N_3\varepsilon_3 + ...}{N} = \frac{1}{N}\left[N_1 \times \frac{1}{2}mc_1^2 + N_2 \times \frac{1}{2}mc_2^2 + N_3 \times \frac{1}{2}mc_3^2 + ...\right]$$

$$= \frac{1}{2}m\left(\frac{N_1c_1^2 + N_2c_2^2 + N_3c_3^2 + ...}{N}\right) = \frac{1}{2}m\,c_{RMS}^2 .$$

The term within the bracket is called c_{RMS}^2 (mean-square-speed, $\overline{c^2}$) and root-mean-square speed is defined as

$$c_{RMS}\left(=\sqrt{\overline{c^2}}\right) = \sqrt{\frac{N_1c_1^2 + N_2c_2^2 + N_3c_3^2 + ...}{N}}$$

Concept of Temperature and Kinetic Theory

This speed $\left(c_{RMS}\right)$ is more fundamental than average speed, $\bar{c}$ since it originates spontaneously from the average kinetic energy of the molecules and it depends on the thermodynamic parameter, temperature (T)
(Postulate 7).

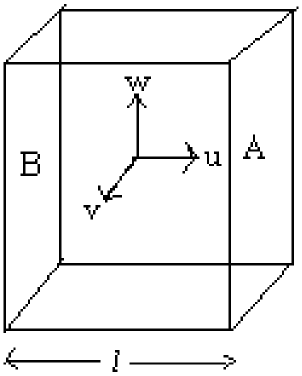
Thus kinetic theory of gases can provide a concept of temperature (T). Average kinetic energy $\left(\bar{\varepsilon}\right)$ is a measure of temperature. Higher the average kinetic energy of a gas, greater will be its temperature. When the molecules are at rest (i.e. $\bar{\varepsilon}$ = 0), the temperature will also be 0 K.

Formulation of kinetic equation, $PV = \frac{1}{3} m N c_{RMS}^2$

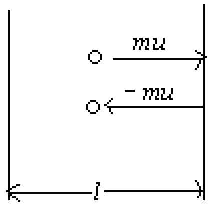
These postulates are used to formulate the above kinetic equation Let us take a cube of edge length l containing N molecules of a gas of molecular mass m and RMS speed is c at temperature T and pressure P. Let N_1 molecules have speed c_1, N_2 molecules have speed c_2 , N_3 molecules have speed c_3 and so on.

Let us concentrate our attention to a single molecule among N_1 that have resultant speed c_1 and the component velocities are u, v and w along the x-, y- and z-axes respectively, so that

$$c_1^2 = u^2 + v^2 + w^2$$



Volume of the cube, V = l^3
Total surface area = $6l^2$



Change of momemtum for the collision = $mu - (-mu) = 2mu$

The molecule will collide walls A and B with the component velocity u and other opposite faces by v and w. Change of momentum of the molecule along x- direction for a single collision = $mu - (-mu) = 2mu$.

The number of collisions suffered by the molecule in one sec between the two opposite walls = $\frac{u}{l}$ and so the rate of change of momentum for the above type collisions = $2mu \times \frac{u}{l} = \frac{2mu^2}{l}$. Similarly along y- and z- directions, the rate of change of momenta of the molecule are $\frac{2mv^2}{l}$ and $\frac{2mw^2}{l}$ respectively.

Total rate of change of momentum of the molecule = $\frac{2m}{l}\left(u^2 + v^2 + w^2\right) = \frac{2mc_1^2}{l}$. For similar N_1 molecules, the rate of change of momentum = $\frac{2mN_1c_1^2}{l}$. Taking all the molecules of the gas, the total rate of change of momentum = $\frac{2mN_1c_1^2}{l} + \frac{2mN_2c_2^2}{l} + \frac{2mN_3c_3^2}{l} + ... = \frac{2mN}{l}\left(\frac{N_1c_1^2 + N_2c_2^2 + N_3c_3^2 + ...}{N}\right) = \frac{2mN\overline{c^2}}{l}$.

According to the Newton's 2nd law of motion, rate of change of momentum due to wall-collision is equal to the force developed on the walls of the gas container. That is $P \times 6l^2 = \frac{2mN\overline{c^2}}{l}$ but, $l^3 = V$, volume of the gas in the cube. So the kinetic equation of the gas is

$$P \times V = \frac{1}{3} mN\overline{c^2} \qquad \text{--(1)}$$

Again the equation is $P = \frac{1}{3}\left(\frac{mN}{V}\right)\overline{c^2}$ but, $\frac{mN}{V} = d$, density of the gas at the given temperature and pressure.

So, another form of the kinetic equation is $P = \frac{1}{3}d\overline{c^2}$. This c is RMS speed of the gas molecules.

These equations are also valid for any shape of the gas container other than cubic one.

Expression of root-mean-square speed

Let us apply the kinetic equation for 1 mole ideal gas. In that case, $mN = mN_A = M$, the molar mass of the gas and the ideal gas equation for 1 mole is PV = RT.

Putting in the kinetic equation, we have $RT = \frac{1}{3}Mc^2$. So root-mean-square speed,

$$c\left(=\sqrt{\overline{c^2}}\right) = \sqrt{\frac{3RT}{M}} .$$

This shows that RMS speed depends on the molar mass (M) and temperature (T) of the gas.

Problem: Calculate the RMS speed of O_2 gas molecules at 27 ^oC. **[Ans. 483 m/s]**

Expression of average kinetic energy ($\bar{\varepsilon}$)

Again, the kinetic equation can be written as $P \times V = \frac{2}{3}N\left(\frac{1}{2}mc^2\right)$, but $\frac{1}{2}mc^2 = \bar{\varepsilon}$, average kinetic energy of the molecules. So, $PV = \frac{2}{3}N\bar{\varepsilon}$. -- (2).

Thus considering 1 mole ideal gas, $RT = \frac{2}{3}N_A \times \bar{\varepsilon}$ or, $\bar{\varepsilon} = \frac{3}{2}\left(\frac{R}{N_A}\right)T$ or, $\bar{\varepsilon} = \frac{3}{2}kT$, ---------------------- (3)

where k is the Boltzmann constant $\left(\frac{R}{N_A}\right)$ $=1.38 \times 10^{-16}$ erg molecule^{-1} K^{-1}.

For 1 mole gas, the KE is $\bar{E} = \frac{3}{2}RT$ and for n mole of the gas, the KE is $E = \frac{3}{2}nRT$.

$\bar{\varepsilon}$ depends on the temperature only and does not depend on the nature of the gas. Thus, most light gas H_2 and very heavy gas UF_6 both have same average kinetic energy at a given temperature.

Problem: Calculate the kinetic energy of translation of 8.5 gm of ammonia gas at 27 ^oC. **[Ans. 450 cal]**

Problem: Which of the following statement(s) is (are) true?

In kinetic theory of gases,

(A) Average kinetic energy of the molecules is proportional to absolute temperature.

(B) The rms velocity at a given temperature is inversely proportional to the square root of molecular mass.

(C) The pressure exerted by the gas is one third of the kinetic energy per unit volume.

(D) If the pressure is isothermally doubled, rms speed is doubled. **[IIT – JAM, 2015, MSQ Type]**

Correct Options are (A) and (B).

Deduction of the gas laws from kinetic equation:

From kinetic equation (2), we have $PV = \frac{2}{3} N \bar{\varepsilon}$ but, $\bar{\varepsilon} \propto T$ (Postulate 7) or, $\bar{\varepsilon} = k'T$

or, $PV = \left(\frac{2}{3} N k'\right) T$ = constant × T. This equation provides necessary deduction of the gas laws such as Boyle's law, Charle's law, etc. Deduction of the Avogadro's law is given here only.

Let us consider two gases under same T, P and V. Thus, $PV = \frac{1}{3} m_1 N_1 c_1^2 = \frac{1}{3} m_2 N_2 c_2^2$

$$\text{or, } m_1 N_1 c_1^2 = m_2 N_2 c_2^2 . \qquad \text{(a)}$$

Again, the two gases have the same average KE at the given T, so $\bar{\varepsilon}_1 = \bar{\varepsilon}_2$ or, $\frac{1}{2} m_1 c_1^2 = \frac{1}{2} m_2 c_2^2$

$$\text{or, } m_1 c_1^2 = m_2 c_2^2 . \qquad \text{(b)}$$

So dividing the equation (a) by the equation (b), we have $N_1 = N_2$.
It means that equal volumes of all gases at the same T and P contain equal number of molecules and it is Avogadro's law.
Graham's law of diffusion can also be deduced. The rate of diffusion of a gas (r_d) is directly proportional to the speed of the gas. That is, $r_d \propto c$ but, $c = \sqrt{\frac{3RT}{M}}$ so, $r_d \propto \sqrt{\frac{3RT}{M}}$. This shows that at a given T, $r_d \propto \sqrt{\frac{1}{M}}$.
Thus, at a given temperature, the rate of diffusion is inversely proportional to the square root of molar mass of the gas and this is Graham's law of diffusion.

Problem (1): For one mole of a monatomic ideal gas, the relation between pressure (P), volume (V) and average molecular KE $\left(\bar{\varepsilon}\right)$ is

(A) $P = \frac{N_A \bar{\varepsilon}}{V}$ (B) $P = \frac{N_A \bar{\varepsilon}}{3V}$ (C) $P = \frac{2N_A \bar{\varepsilon}}{3V}$ (D) $P = \frac{2N_A}{3V\bar{\varepsilon}}$ **[GATE 2000]**

Answer: (C).

Problem (2): Two gases A and B have equal volume, equal number of mole and equal r m s speed but unequal molar masses $M_A > M_B$. Which gas has higher pressure and why? [**Burdwan Univ. 2008]**

Solution: Hints: We have for ideal gas, PV = nRT and $c_{rms} = \sqrt{\frac{3RT}{M}}$ or, $RT = \frac{M}{3} c_{rms}{}^2$.

Thus $PV = n \times \frac{M}{3} c_{rms}{}^2$ or, $P = \left(n \times \frac{c_{rms}{}^2}{3V}\right) M$ = constant × M.

This shows that the gas A has higher pressure than the gas B.

Problem (2): At what temperature will the r m s velocity of oxygen gas be one and half times its value at NTP?

Solution: Temperature is 619.25 K **[Burdwan Univ. 2015]**

Problem (3): Compare the rates of effusion of methane and of sulphur dioxide through the same pin-hole at the same temperature if the pressure of sulphur dioxide is four times than of methane.

[Burdwan Univ. 2015]

Solution: $\left(r_e\right)_{CH_4} \propto \sqrt{\frac{T}{M}} = \sqrt{\frac{T}{16}}$ and $\left(r_e\right)_{SO_2} \propto \sqrt{\frac{T}{M}} = \sqrt{\frac{T}{64}}$. Thus $\left(r_e\right)_{CH_4} : \left(r_e\right)_{SO_2} = 2$.

[Rate of effusion does not depend on the pressure of the gas.]

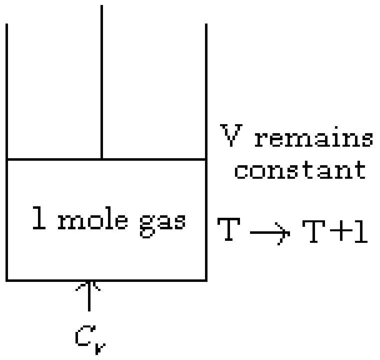
Molar heat capacities of gases

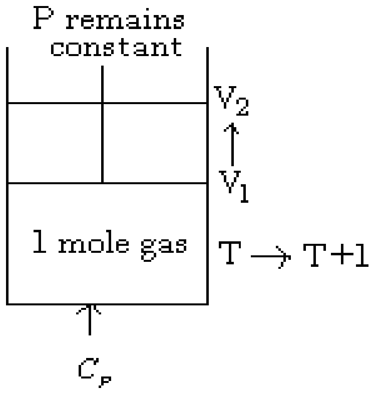
Heat capacity (C) of a substance is defined as the amount of heat required to raise the temperature of the substance by one degree. Heat capacity per gram of a substance is called specific heat and per mole is called molar heat capacity.

Thus molar heat capacity = molar mass × specific heat.

For gases, there are two heat capacities at constant volume and at constant pressure.

So for gases $C_V = M \times c_V$ and $C_P = M \times c_P$, where C_V and C_P are the molar heat capacities at constant volume and at constant pressure 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.

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^o rise in temperature = $\frac{3}{2}R(T+1) - \frac{3}{2}RT = \frac{3}{2}R$.

Let the intramolecular energy increase for the gas for 1^o rise in temperature = x, then $C_V = \frac{3}{2}R + x$

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 ratio (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, for diatomic gas, x = R = 2 cal mol^{-1}K^{-1},

and for polyatomic gas, $x = \frac{3}{2}R$ = 3 cal mol^{-1}K^{-1}.

Thus, γ = 5/3 = 1.66 for monatomic gas, = 7/5 = 1.4 for diatomic gas and = 4/3 = 1.33 for polyatomic gas.

For a gas, γ 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 γ thus provides the atomicity (molecular complexity) of the gas.

Problem: The specific heat at constant pressure and at constant volume is 0.125 and 0.075 cal gm^{-1} K^{-1} respectively. Calculate the molar mass and atomicity of the gas. Name the gas if possible.

[M = 40 gm/mole, γ = 1.66 (monatomic), argon]

Simple concept of probability

When a coin is tossed, either head or tail may be upwards. The probability of the coin for head being up is ½ or 50 %. It means that if we toss the coin twice, then one time the head will be up. However, this may not happen always and hence the idea of probability will be applicable only when large number of operations will be made. Another condition for applicability of the probability is that the two sides of the coin (events) must be equally likely and mutually exclusive. Therefore, the probability (P) is defined as,

$$P = \frac{number\ of\ \ favourable\ events\ (m)}{total\ number\ of\ events\ (n)}.$$

Or, $P = \dfrac{number\ of\ \ favourable\ events\ (p)}{number\ of\ \ favourable\ events\ (p) + number\ of\ unfavourable\ events\ (q)}$ i.e. P $= \dfrac{p}{p+q}$.

The range of probability is from 0 to 1. That is, $0 \le P \le 1$

For a well-shuffled packet of cards, probability of drawing a diamond is 13/52 =1/4 (P_1) and probability of drawing a king = 4/52 = 1/13 (P_2).

But when both conditions are imposed simultaneously i.e., to draw a card which will be a king and also diamond, the probability (P_{12}) = 1/52 = (1/4) × (1/13) = $P_1 \times P_2$, i.e., it is the product of two individual probabilities. Thus, the probability follows multiplicative rule.

For instance, it might be important to know the probability that a system has both the value x_i of some discrete property x and the value y_i of some other discrete property y. If the properties are independent of each other, the probability of the system having both value x_i of the property x and value y_i of the property y is

$$P(x_{i,}\ y_i) = P(x_i) \times P(y_i)$$, where $P(x_i)$ and $P(y_i)$ are the individual probabilities.

For example, in a country if the probability of a person being man is 0.495, and the probability of a person (man or women) being left-handed is 0.01, then the probability of selecting a left-handed man by random choice from a crowd is 0.495 × 0.01 = 0.00 495 or, 495 in 1,00,000 (one lakh). If, however, left-handedness were male characteristics, this calculation would be false.

Distribution function and averaging of physical properties of a system

Distribution

A distribution is the division of a group of things into classes on the basis of a certain property of the system. If we have a thousand balls and five boxes, and place the balls in the boxes in any particular way we like, the result is the distribution. If we divide the people of a country into classes according to age, the result is an age distribution. Such a distribution shows how many people are between the ages (say) of 0 to 5 years, between 5 to 10 years, 10 to 15 years and so on. Similarly we can divide the students in class according to the marks they obtain in an examination within a certain range.

Choice of range or width of the interval

While we distribute a group of things in classes, we generally use range or width of the classification for better computation of the average value. This range or width must be small and not very large. In the above example, let us consider the age distribution in which the range is taken 5 years. Clearly it is absurd to choose 100 years as the width of the interval then the people could not be divided into classes at all. So the width must be small. On the other hand, if we choose a very small interval width say one day, and then in any small group of people, say of 10 people, we find that one person falls in each of the ten intervals and zero falls in all the others. For any large group, the time required to write down such a detailed distribution is just impossible. Therefore, the interval width to be chosen must be wide enough to eliminate details of no interest but narrow enough to display meaningful aspects so that it allows calculating more accurate average value of the property.

Averaging of a property

The distribution is used to compute average value. From the distribution mentioned above, we can compute the age of the people of the country or average marks of the students they obtain, etc.
Let us cite an example to see how the distribution is helpful in averaging the properties of a system. For the average value of a property x, let us take x_1 (outcome of the observation) occurs n_1 times, x_2 occurs n_2 times, x_3 occurs n_3 times and so on. The mean value ($\bar{x}$) of the property x is the weighted sum of all the outcomes divided by the total number of observations.

$$\bar{x} = \frac{n_1x_1 + n_2x_2 + n_3x_3 + ... + n_ix_i}{n_1 + n_2 + n_3 + ... + n_i} = \frac{n_1x_1 + n_2x_2 + n_3x_3 + ... + n_ix_i}{n} .$$

We can write the computation in different way in terms of probability (P) also.

$$\bar{x} = \left(\frac{n_1}{n}\right)x_1 + \left(\frac{n_2}{n}\right)x_2 + \left(\frac{n_3}{n}\right)x_3 + ... + \left(\frac{n_i}{n}\right)x_i = P(x_1)x_1 + P(x_2)x_2 + P(x_3)x_3 + ... + P(x_i)x_i = \Sigma P(x_j)\,x_j ,$$

where $P(x_j)$ is the probability of outcome of the property, x_j in the sample.

But if the outcome of an experiment may take continuous values like the case of height of a population or in the speed of gas molecules, then the definition of the mean value has to be modified. Summation will be replaced by integration and the mean value can be written as

$$\bar{x} = \int\limits_{\substack{all\ possible \\ values\ of\ x}} x\ f(x)\,dx ,$$

where $f(x)\,dx$ = P(x), the probability for the outcome of x lies some where within the infinitesimal range dx at x i.e., from x to $x + \mathrm{d}\,x$, where $f(x)$ is the **distribution function.**

Distribution function:

In the above, this analytical expression $f(x)$ is called distribution function or probability density of the property, x. It may be defined as $f(x) = \dfrac{P(x)}{dx}$ but, $P(x) = \dfrac{dn_x}{n}$. Thus the distribution function is written as $f(x) = \dfrac{1}{n}\left(\dfrac{dn_x}{dx}\right)$. It is defined as probability of the outcome x within unit range at x.

For the mean height of a population, $\bar{h} = \int\limits_0^\infty h\ f(h)\,dh$, because only (+ve) values of h are possible and thus, the limit of h ranges from 0 to ∞. If we consider the mean velocity of molecules in x- direction, then

$$\bar{u} = \int\limits_{-\infty}^{+\infty} u\ f(u)\,du .$$

For example, $f(h)dh = P(h)$, probability of a person to have height h to $h + dh$ and $f(h) = \dfrac{1}{n}\left(\dfrac{dn_h}{dh}\right)$. Thus $f(h)$ tells us the probability of a height h within unit range at h.

If $f(180\ cm) = 0.12\ cm^{-1}$, we would know that the probability of the height of a sample of population falling in the range 180 – 181 cm is approximately 0.12 or 12 % and that for the range 180 – 182 cm is approximately 0.24 or 24 %. However, if the height chosen at 200 cm, then it may be that $f(200\ cm) = 0.01\ cm^{-1}$ which means that the probability of the height in the range 200 – 201 cm is only about 0.01 or 1 %. So the distribution severely depends on the location of the value.

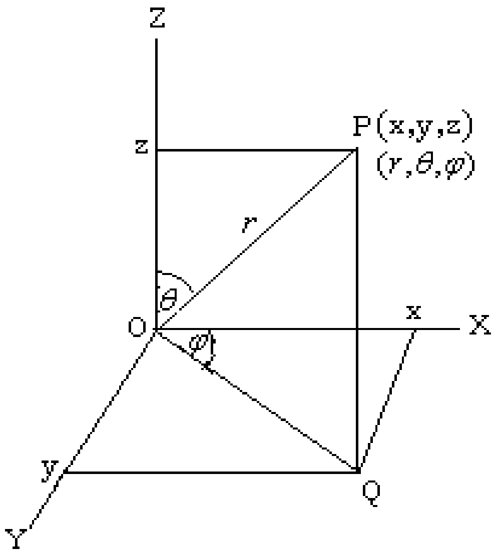
This suggests that the distribution function $f(h)$ depends strongly on the location of the value, here h.

Multiplicative nature of the probability can be shown for continuous properties also. If the probability of x lying in the range dx at x is $f(x)\,dx$, and the probability that an independent property y lies in the range dy at y is

$f(y)\,dy$, then the probability of x lying in the range x to $x+dx$ and y in y to $y+dy$ is the product of probabilities : $f(x)\,dx \times f(y)\,dy$ or $f(x)\,f(y)\,dx\,dy$.

Conversion between Cartesian co-ordinates and Polar co-ordinates

Description of the co-ordinates: Co-ordinates are used to locate a point in space. There are two types co-ordinate systems. These are shown by the adjoining diagram. In the Cartesian co-ordinate system, the point P is designated by the co-ordinates (x, y, z) and in the polar system, the co-ordinates are (r, θ, φ).



To identify the co-ordinates of the point P, a perpendicular is drawn from point P on the Z-axis and it cuts at z. Another perpendicular is drawn on the XY plane and it cuts at Q point on the plane.

Then perpendiculars are drawn from Q on the X-axis and Y-axis and these cut at x and y. These (x, y, z) are the co-ordinates of the point P in the Cartesian system.

In the polar system, the point P is designated by (r, θ, φ). The distance between O and P is r, called radial distance. This radial distance OP makes an angle, θ with Z-axis. This angle is called zenith angle. Again, OQ makes an angle, φ with the X-axis and this angle is called azimuthal angle.

Range of each x, y, z co-ordinates are from $-\infty$ to $+\infty$.

the range of r is from 0 to ∞, θ from 0 to π and φ from 0 to 2π.

Conversion between the two systems

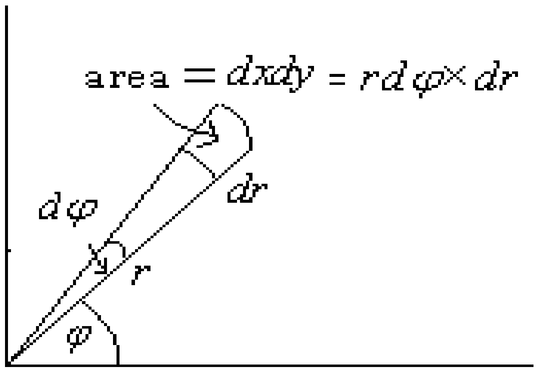
$OQ = OP\cos(90-\theta) = r\sin\theta$. Now the Cartesian co-ordinates are deduced as follows:

$z = r\cos\theta$, $x = OQ \times \cos\varphi = r\sin\theta\cos\varphi$ and $y = OQ \times \cos(90-\varphi) = r\sin\theta\sin\varphi$. So conversion from polar co-ordinates to Cartesian co-ordinates is given as, $x = r\sin\theta\cos\varphi$, $y = r\sin\theta\sin\varphi$ $z = r\cos\theta$,

Conversion from Cartesian co-ordinates to polar co-ordinates is given as follows:

Radial distance, $r = \sqrt{x^2+y^2+z^2}$, zenith angle, $\theta = \cos^{-1}\left(\dfrac{z}{\sqrt{x^2+y^2+z^2}}\right)$ and azimuthal angle $\varphi = \tan^{-1}\left(\dfrac{y}{x}\right)$.

Conversion of area $dxdy$ and volume $dxdydz$ in polar co-ordinates are shown by diagram only.



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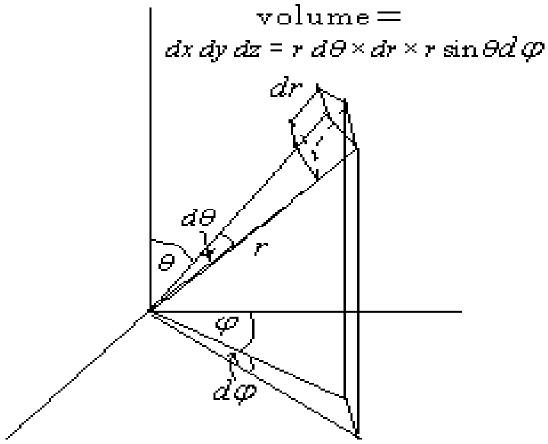


Properties of Gamma function

Definition

A limited definition of gamma (Γ) function is given by the integral, $\Gamma(n)=\int_0^\infty t^{n-1}e^{-t}dt$ for $n>0$.

Reduction formula of $\Gamma(n)$

The Gamma function of n can be degraded by the following way.

Integrating by parts it gives

$$\Gamma(n)=\int_0^\infty t^{n-1}e^{-t}dt=\left[-t^{n-1}e^{-t}\right]_0^\infty+(n-1)\int_0^\infty t^{n-2}e^{-t}dt=0+(n-1)\int_0^\infty t^{n-2}e^{-t}dt=(n-1)\Gamma(n-1)\,.$$

Thus, $\Gamma(n)=(n-1)\Gamma(n-1)$.

Repeated successive integration by parts leads to following cases:

case I: When n is (+ve) integer

$$\Gamma(n)=(n-1)\Gamma(n-1)=(n-1)(n-2)\Gamma(n-2)=(n-1)(n-2)(n-3)\Gamma(n-3)$$
$$=(n-1)(n-2)(n-3)......3\times2\times1\times\Gamma(1).$$

Evaluation of $\Gamma(1)$

By definition, $\Gamma(1)=\int_0^\infty t^0e^{-t}dt=\left[-e^{-t}\right]_0^\infty=\left[e^{-t}\right]_\infty^0=1-0=1$, Thus, $\Gamma(1)=1$

Therefore, $\Gamma(n)=(n-1)(n-2)(n-3)......3\times2\times1=(n-1)!.$

This leads to the formulation,

$$\Gamma(2)=\int_0^\infty t\,e^{-t}dt=1!=1,\quad \Gamma(3)=\int_0^\infty t^2\,e^{-t}dt=2!=2,\quad \Gamma(4)=\int_0^\infty t^3\,e^{-t}dt=3!=6.$$

Evaluation of $0!$: The above formulation gives that $0!=\Gamma(1)=1$.

Case II: When n is half an odd integer

$$\Gamma(n)=(n-1)(n-2)(n-3)......(3/2)\times(1/2)\times\Gamma(1/2)\,.$$

Evaluation of $\Gamma(1/2)$

For this purpose, let us first evaluate the integral, $I=\int_0^\infty e^{-x^2}dx$.

Then, $I^2=\int_0^\infty e^{-x^2}dx\times\int_0^\infty e^{-x^2}dx=\int_0^\infty e^{-x^2}dx\times\int_0^\infty e^{-y^2}dy=\int_0^\infty\int_0^\infty e^{-\left(x^2+y^2\right)}dx\,dy=\int_0^\infty\int_0^{\pi/2} e^{-r^2}r\,dr\,d\varphi$.

The variation of φ is limited from 0 to $\pi/2$ since x and y are in the range over positive values only (first quadrant). Thus,

$I^2=\int_0^\infty e^{-r^2}r\,dr\int_0^{\pi/2}d\varphi=\frac{1}{2}\times\frac{\pi}{2}=\frac{\pi}{4}$ or, $I=\frac{1}{2}\sqrt{\pi}$. [For the integral, $\int_0^\infty e^{-r^2}r\,dr$, let $r^2=x$ and so $2\,r\,dr=dx$, putting we get the integral, $\int_0^\infty e^{-r^2}r\,dr=\frac{1}{2}\int_0^\infty e^{-x}dx=-\frac{1}{2}\left[e^{-x}\right]_0^\infty=\frac{1}{2}$.]

Now we find the value of $\Gamma(1/2)$. We have $\frac{1}{2}\sqrt{\pi}=\int_0^\infty e^{-x^2}dx$, let $x^2=t$ or, $2x\,dx=dt$ or, $2\sqrt{t}\,dx=dt$

or, $dx = \frac{1}{2}\frac{dt}{\sqrt{t}}$. So, $\frac{1}{2}\sqrt{\pi} = \frac{1}{2}\int_0^\infty t^{-1/2}\, e^{-t}dt = \frac{1}{2}\int_0^\infty t^{\left(\frac{1}{2}-1\right)} e^{-t}dt = \frac{1}{2}\Gamma\left(\frac{1}{2}\right)$ or, $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$.

Hence for n = half of an odd integer, we can find the values,

$$\Gamma(n) = (n-1)(n-2)(n-3)......(3/2)\times(1/2)\times\Gamma(1/2) = (n-1)(n-2)(n-3)......(3/2)\times(1/2)\times\sqrt{\pi}$$

i.e., $\int_0^\infty t^{n-1}e^{-t}dt = (n-1)(n-2)(n-3)......(3/2)\times(1/2)\times\sqrt{\pi}$. This formulation gives the value,

$$\Gamma(5/2) = (3/2)(1/2)\Gamma(1/2) = (3/2)(1/2)\sqrt{\pi} = (3/4)\sqrt{\pi} \text{ .}$$

Case III: When n = (+ve) quantity but other than an integer or half of an odd integer, integration is not so easy.

Application of gamma function

(1) Evaluation of the integral, $\int_0^\infty x^n e^{-ax}dx$, when n = (+ve) integer.

Let $ax = t$ or, $adx = dt$ or, $dx = \frac{1}{a}dt$, putting these values, we have integration

$$\int_0^\infty x^n e^{-ax}dx = \int_0^\infty \left(\frac{t}{a}\right)^n e^{-t}\times\frac{1}{a}dt = \frac{1}{a^{n+1}}\int_0^\infty t^n\, e^{-t}dt = \frac{1}{a^{n+1}}\Gamma(n+1) = \frac{n!}{a^{n+1}} \text{ .}$$

Thus, $$\int_0^\infty x^n e^{-ax}dx = \frac{n!}{a^{n+1}}$$

Example : When n = (+ve) integer (say 2)

$$\int_0^\infty x^2 e^{-ax}dx = \frac{\Gamma(3)}{a^3} = \frac{2!}{a^3} = \frac{2}{a^3} \text{ .}$$

(2) Evaluation of integral, $\int_0^\infty x^n e^{-bx^2}dx$, when n = (+ve) integer or zero.

Let $bx^2 = t$ or, $2bxdx = dt$ or, $2b\left(\frac{t}{b}\right)^{1/2}dx = dt$ or, $dx = \frac{1}{2b}\times\left(\frac{b}{t}\right)^{1/2}dt$. The integral is thus,

$$\int_0^\infty x^n e^{-bx^2}dx = \int_0^\infty\left(\frac{t}{b}\right)^{n/2} e^{-t}\times\frac{1}{2b}\left(\frac{b}{t}\right)^{1/2}dt = \frac{1}{2b^{\frac{n}{2}+1-\frac{1}{2}}}\int_0^\infty t^{\left(\frac{n}{2}-\frac{1}{2}\right)}e^{-t}dt = \frac{1}{2\sqrt{b^{n+1}}}\int_0^\infty t^{\frac{n-1}{2}}e^{-t}dt$$

$$= \frac{1}{2\sqrt{b^{n+1}}}\int_0^\infty t^{\frac{n+1}{2}-1}e^{-t}dt = \frac{1}{2\sqrt{b^{n+1}}}\Gamma\left(\frac{n+1}{2}\right)$$. Thus the integral is $\int_0^\infty x^n e^{-bx^2}dx = \frac{1}{2b^{\frac{n+1}{2}}}\Gamma\left(\frac{n+1}{2}\right)$.

Example (a): When n = (+ve) even integer (say 2)

$$\int_0^\infty x^2 e^{-bx^2}dx = \frac{1}{2b^{\frac{3}{2}}}\Gamma\left(\frac{3}{2}\right) = \frac{1}{2\sqrt{b^3}}\times\frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{1}{4}\frac{\sqrt{\pi}}{\sqrt{b^3}} = \frac{1}{4}\sqrt{\frac{\pi}{b^3}} \text{ .}$$

Example (b): When n = (+ve) odd integer (say 3)

$$\int_0^\infty x^3 e^{-bx^2}dx = \frac{1}{2b^2}\,\Gamma(2) = \frac{1}{2b^2}\times 1 = \frac{1}{2b^2} \text{ .}$$

Various standard integrals can be done easily by the use of this Gamma function.

Maxwell distribution of speeds

Introduction

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. Particles refer to gaseous atoms or molecules but in this text, we shall use molecules only.

On the basis of probabilistic idea, Maxwell and later Boltzmann formulated the distribution law as

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

where $\frac{dn_c}{n}$ is the fraction of molecules that have speed c to $c+dc$, m is the molecular mass of the gas and T is the temperature in absolute scale.

Assumptions

The following assumptions are made for the distribution of the molecular speeds.

(1) The number density of molecules (i.e., number of molecules per unit volume) is uniform through out the gas assembly in the ideal gaseous system at thermodynamic equilibrium and at given temperature (T).

(2) The motion of the molecules is complete random. They move in all directions with equal probability. This is isotropic behavior of the molecular motion.

(3) The resultant speed of the molecule (c) can be resolved into three mutually perpendicular component velocities u, v and w, such that

$$c^2 = u^2 + v^2 + w^2 .$$

These component velocities are equally likely and mutually exclusive. Maxwell also assumed that these component velocities are independent to one another.

(4) Though the speeds are changing due to intermolecular collisions, yet at a given temperature, definite fraction of the molecules will always have definite speed within a small range. This situation is called the steady state condition of the molecular speeds of the gas at temperature, T.

(5) The distribution of speeds will be disturbed if any internal force field (such as intermolecular attraction in real gases) or external force field (such as gravitational force field) is operative in the gas.

In brief, 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.

Formulation

Let us first consider the motion of the molecules in the x- direction with velocity u. The probability of a molecule to have velocity, u within range du is given by $P(u)$. This probability is increased with the increase of range, du and it also depends on the location of u at which the range is considered. Thus, the probability of a molecule that have velocity u within range du is given by,

$$P(u) = f(u)\,du .$$

The probability, $P(u)$ depends on some function of u i.e., $f(u)$ and this function is some mathematical form which contains u.

Since u, v and w are equally likely for the molecule, hence the probability of a molecule to have velocity v and w within the range dv and dw are respectively,

$$P(v) = f(v)\,dv \quad \text{and} \quad P(w) = f(w)\,dw$$

The mathematical format of the functions, $f(u)$, $f(v)$ and $f(w)$ are same, except $f(u)$ contains u, $f(v)$ contains v and $f(w)$ contains w only.

Since, u, v and w are equally likely and mutually exclusive, the probability of a molecule to have the velocity u to $u+du$, v to $v+dv$ and w to $w+dw$ simultaneously is

$$P(uvw) = P(u)\times P(v)\times P(w) = f(u)\,du \times f(v)\,dv \times f(w)\,dw$$

or,

$$P(uvw) = f(u)\,f(v)\,f(w)\,du\,dv\,dw .$$

But, $P(uvw)=\frac{dn_{uvw}}{n}$, then $\frac{dn_{uvw}}{n}=f(u)\,f(v)\,f(w)\,du\,dv\,dw$, where dn_{uvw} is the number of molecules out of total number n that have velocities u, v and w simultaneously within range du, dv and dw.

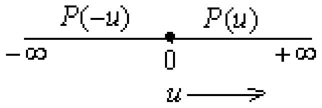
Thus, $\frac{dn_{uvw}}{n}=F(u,v,w)\,du\,dv\,dw$, where $F(u,v,w)=f(u)\,f(v)\,f(w)$

and $F(u,v,w)$ is the probability density or distribution function that contains u, v and w terms.

Isotropic nature of molecular motion

Now we consider the function, $P(u)=f(u)\,du$ and $P(u)$ is the probability of the molecule that have velocity u within range du in the x- directional motion of the molecule.

Since the molecular motion is isotropic in nature, the probability of a molecule to have velocity u to $u+du$ in the range 0 to $+\infty$ is same with that in the range 0 to $-\infty$. This aspect of the molecular motion is possible if the function $f(u)$ contains u^2 and not u. If the function contains u, then $P(u)$ becomes different for the molecule to have velocity u and $-u$ within the same range du. In that case, the molecule has not the same chance of going east with certain velocity as it has the chance of going west with that velocity. But if the function may contain u^2, the probability of the above motions becomes same and isotropicity is maintained and as in the figure, $P(u)$ must be same with $P(-u)$.



Evaluation of nature of the function

Considering the isotropicity of molecular motion, the functions may be written as $f(u^2)$, $f(v^2)$ and $f(w^2)$. Then, $F(u,v,w)$ will be $F(u^2,v^2,w^2)$ and it is the probability density or distribution function of molecules to have velocities u, v,

In the adjacent velocity space diagram, let the point P is the position of molecules that have component velocities u, v, w and the resultant speed c such that

$$c^2=u^2+v^2+w^2 .$$

The molecules that have velocities u, v and w within range du, dv and dw must have the velocity points within the rectangular box of volume, $du\,dv\,dw$ at that point P.

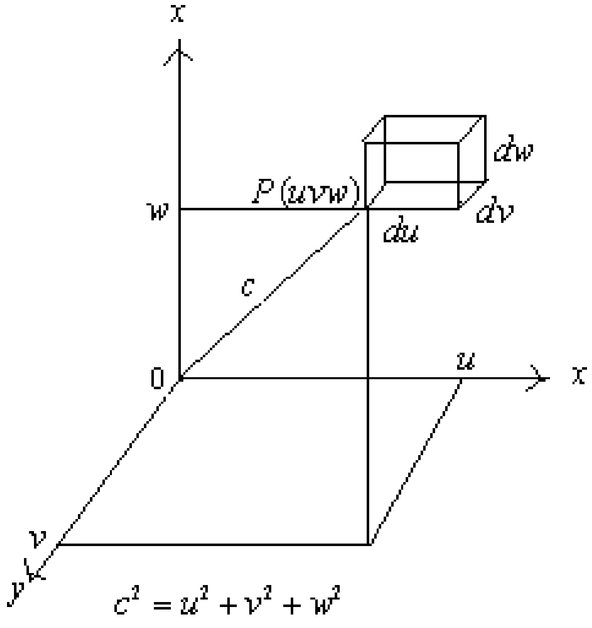
Thus the probability density or distribution function,

$$f(u^2)\,f(v^2)\,f(w^2)=F(c^2)=F(u^2+v^2+w^2)$$

or, $f(u^2)\,f(v^2)\,f(w^2)=F(u^2+v^2+w^2)$

This mathematical condition can only be satisfied by the exponent function [such as $e^a\times e^b\times e^c=e^{(a+b+c)}$].

Then let each function may be written as $f(u)=Ae^{\pm bu^2}$, where A and b are constants dependent on the nature of the gas and temperature.



Velocity distribution in Cartesian co-ordinates

Again, $f(u)$ is the probability of the molecule to have velocity virtually u, hence it can have only finite value.

But, if (+ve) sign in the exponent term is taken, then when $u\to\infty$, $f(u)$ becomes infinite which is not possible.

Thus, only ($-$ve) sign is allowed and the function is $f(u)=Ae^{-bu^2}$. Other functions are thus $f(v)=Ae^{-bv^2}$ and $f(w)=Ae^{-bw^2}$. Then the distribution law in Cartesian co-ordinates is given as

$$\frac{dn_{uvw}}{n} = f(u)\,f(v)\,f(w)\,du\,dv\,dw = A^3 e^{-b\left(u^2+v^2+w^2\right)} du\,dv\,dw$$

or, $$\frac{dn_{uvw}}{n} = A^3 e^{-bc^2} du\,dv\,dw\,.$$

Distribution function in polar co-ordinates

The above equation can be converted into polar co-ordinates by replacing $du\,dv\,dw = c^2 dc \sin\theta d\theta\, d\varphi$ and thus the distribution in polar co-ordinates is

$$\frac{dn_{c\theta\varphi}}{n} = A^3 e^{-bc^2} c^2 dc \sin\theta d\theta\, d\varphi\,,$$

where $dn_{c\theta\varphi}$ is the number of molecules that have speed c to $c+dc$ within the angle θ to $\theta+d\theta$ and φ to $\varphi+d\varphi$. If we consider the magnitude of the speed only irrespective of direction, then angle terms are to be integrated with the full range of θ and φ i.e.,

$$\frac{dn_c}{n} = A^3 e^{-bc^2} c^2 dc \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi\ ,$$

where dn_c is the number of molecules out of n that have speed c to $c+dc$ in any direction. Integrating and putting the limits, we have $\frac{dn_c}{n} = 4\pi A^3 e^{-bc^2} c^2 dc$ = F (c) dc,

where F (c) = $\frac{1}{n}\frac{dn_c}{dc} = 4\pi A^3 e^{-bc^2} c^2$ and it is the speed distribution function or probability density function that have speed c within unit range of c i.e., c to $c+1$. Since $c >> 1$, so F(c) is practically the fraction of molecules that have speed c.

Evaluation of constant A in terms of b

The value of A can be obtained by the use of normalization condition of F(c) and the condition is $\int_{all\ values\ of\ c} F(c)dc = 1$ or, $\int_{all\ values\ of\ c} \frac{dn_c}{n} = 1$ so, $4\pi A^3 \int_0^{\infty} e^{-bc^2} c^2 dc = 1$

or, $4\pi A^3 \times \frac{\Gamma(3/2)}{2b^{3/2}} = 1$ or, $4\pi A^3 \times \frac{1}{2b^{3/2}}.\frac{1}{2}\sqrt{\pi} = 1$ or, $A^3 \times \left(\frac{\pi}{b}\right)^{3/2} = 1.$

The value of A in terms of b is then $A = \left(\frac{b}{\pi}\right)^{1/2}$ and the speed distribution is $\frac{dn_c}{n} = 4\pi\left(\frac{b}{\pi}\right)^{3/2} e^{-bc^2} c^2 dc$

Evaluation of b

For evaluation of b, let us borrow the value of mean-square speed, $\overline{c^2} = 3kT/m$ from kinetic theory of gas and equate it with the value obtained by averaging from the distribution law.

$$\overline{c^2} = \int_0^{\infty} c^2 \frac{dn_c}{n} = \int_0^{\infty} c^2 \times 4\pi\left(\frac{b}{\pi}\right)^{3/2} e^{-bc^2} c^2 dc = 4\pi\left(\frac{b}{\pi}\right)^{3/2} \int_0^{\infty} c^4 \times e^{-bc^2} dc = 4\pi\left(\frac{b}{\pi}\right)^{3/2} \times \frac{\Gamma(5/2)}{2b^{5/2}}$$

$$= 4\pi\left(\frac{b}{\pi}\right)^{3/2} \times \frac{3}{8}\sqrt{\frac{\pi}{b^5}} = \frac{3}{2}\times\frac{1}{b}$$ and this is equal to $3kT/m$. Thus, $\frac{3}{2}\times\frac{1}{b} = 3kT/m$ or, $b = \frac{m}{2kT}$.

Putting the values of A and b we get the Maxwell distribution of molecular speeds

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

The law can also be written as $\frac{dn_c}{n} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mc^2/2RT} c^2 dc = F(c)\,dc$,

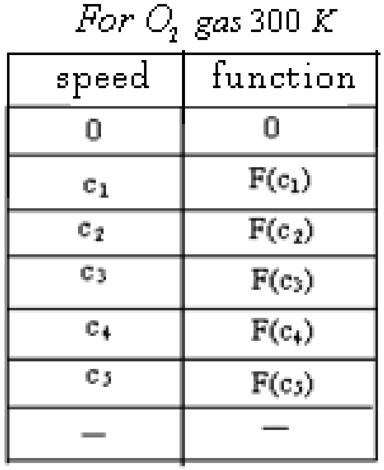
where $F(c) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} c^2$ or, $F(c) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mc^2/2RT} c^2$ and $F(c) = \frac{1}{n}\left(\frac{dn_c}{dc}\right)$, it is the probability of a molecule to have speed c within unit range.

Distribution and dependent factors

From the expression of $F(c)$, it is seen that it depends on the nature of the gas which is characterized by molar mass (M) and the temperature (T). More precisely, $F(c)$ depends on M/T of the gas. Thus, $F(c)$ of O_2 gas molecules at 300 K is same as that of SO_2 gas molecules at 600 K as 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 temperature as both the gases have same molar mass.

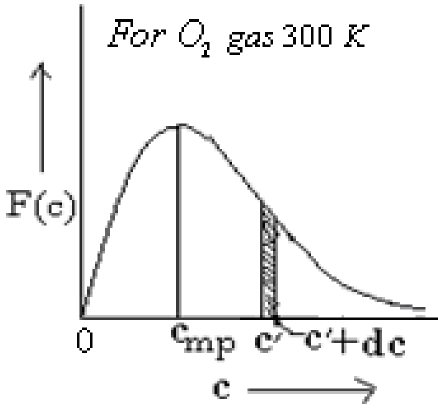
Salient features of the speed distribution law

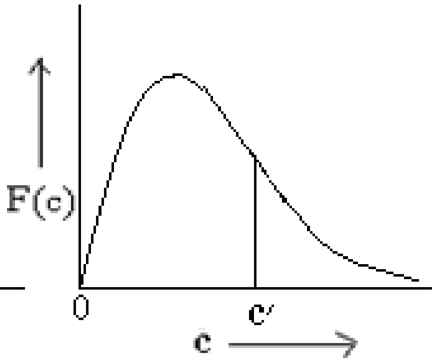
It is possible to calculate $F(c)$ of a particular gas at a given temperature with different speeds ranging from small value to high value. The calculated values can be put in a table and then it can be projected in a figure, $F(c)$ vs. c. These are shown below.



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	$F(c_4)$
c_5	$F(c_5)$
—	—





Various conclusions can be drawn from the mysterically hidden information in the $F(c)$ vs. c curve.

(1) When $c = 0$, $F(c) = 0$ and it means that there is no molecule that have zero speed i.e. no molecule is at rest at any temperature, all molecules are moving in the gaseous phase.

(2) The expression of $F(c)$ contains two factors, one is exponential term, $e^{-mc^2/2kT}$ 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 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 towards asymptotic value with increase of c.
The value of $F(c)$ again becomes zero at $c \to \infty$.

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

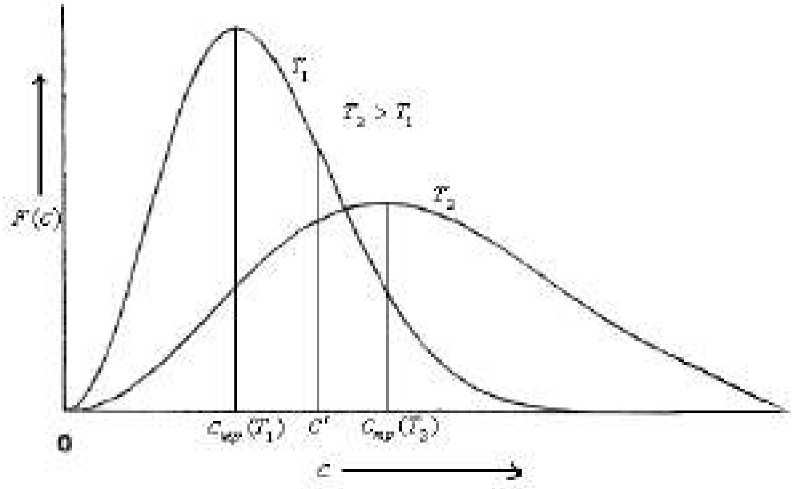
(4) The fraction of the molecules that have speed c' to $c'+dc$ is given by the area, $F(c')\times dc$ (shaded area in the curve). Total area of the curve is unity i.e., fraction of molecules that have speed 0 to ∞ is one.

(5) The fraction of molecules having speed $\geq c'$ is obtained from the area of the right-hand side of the ordinate drawn at c'. Similarly, the fraction of molecules having speed $\leq c'$ is obtained from the area of the left-hand side of the ordinate at c'.

Effect of temperature on the distribution

(1) $F(c)$ also contains two factors which are dependent of T, one is the exponential term, $e^{-mc^2/2kT}$ and the other is non-exponential term, $\left(m/2\pi kT\right)^{3/2}$. At low T, exponential term is low and non-exponential term is high, but at high T, exponential term is high and non-exponential term is low. Thus at low T, as c increases, $F(c)$ increases more due to increase of non-exponential term initially but as c further increases, the exponential term dominates due to presence of T and c^2, and the value of $F(c)$ decreases sharply.

Now at high T, $F(c)$ decreases due to decrease of non-exponential term initially but as c is further increased, the exponential term dominates due to presence of T and c^2, and the value of $F(c)$ decreases, attains maximum and then drops to zero slowly as $c\to\infty$ for the presence of c^2 in the term. But due to high T, the exponential term increases and due to c^2 the term decreases. Overall the exponential term lowers the value of $F(c)$ but the lowering is less than that at low T.



Thus, when the temperature of gas is increased, the distribution curve is broadened and it becomes more uniform.

The most-probable speed is increased with rise in temperature though the fraction of molecules having most-probable speed is decreased.

i.e., if $T_2 > T_1$, then $c_{mp}(T_2) > c_{mp}(T_1)$ but, $F\left(c_{mp}\right)\, at\; T_2 < F\left(c_{mp}\right)\, at\; T_1$.

(2) The fraction of molecules having speed $\geq c'$ is increased with rise in temperature and the fraction of molecules having speed $\leq c'$ is decreased.

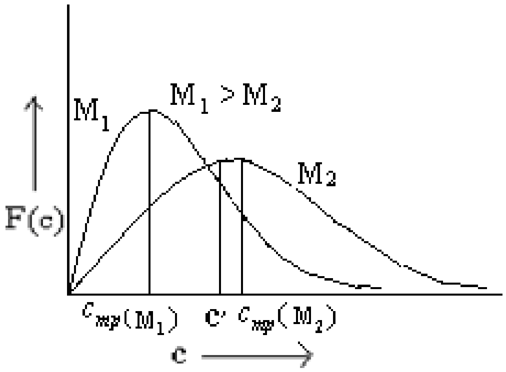
(3) The fraction of molecules having speed close to c_{mp} is also large as the curve is flat at higher T.

(4) If T is more increased, the curve becomes more and more flat and when $T\to\infty$ (very large), 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 is decreased, the curve becomes narrow. More and more T is lowered, the curve becomes more and more narrow and when $T \to 0K$, the curve lies on the $F(c)$ - axis. All the molecules have speed zero and so again the distribution is lost.

(6) However, the total area in both the cases of T_1 and T_2 is same and it is unity.

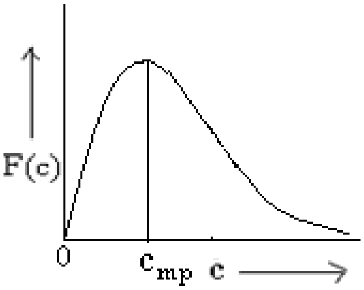
Effect of molar mass on the distribution



The molar mass (M) and temperature (T) remain in the expression of $F(c)$ as $\left(M/T\right)$ so, the effect of M is just the opposite to that of T. Thus the effect of M at constant T, the curve of $F(c)$ vs. c will be similar to that of the effect of T at constant M but in inverse fashion. This is shown in the adjoining figure.
The curve for the gas of lower molar mass (such as helium) is wider than the gas of heavier molar mass (such as argon).

Expression of most-probable speed $\left(c_{mp}\right)$

$F(c)$ attains maximum value at a certain speed in the $F(c)$ vs. c curve and this speed is called most-probable speed, c_{mp}. Using the condition of maxima and minima, $\frac{dF(c)}{dc} = 0$, it is possible to find the expression of c_{mp}.



$$F(c) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} c^2 = A'e^{-mc^2/2kT} c^2 .$$

So, $$\frac{dF(c)}{dc} = A'\left[e^{-mc^2/2kT} \times 2c + c^2 e^{-mc^2/2kT}\left(-\frac{2mc}{2kT}\right)\right] = 0$$

or, $$A'\, 2c\, e^{-mc^2/2kT}\left(1 - \frac{mc^2}{2kT}\right) = 0 .$$

Three options may be considered to find c at which $F(c)$ attains maximum value.

(1) When c = 0, the expression is zero and it is the minimal condition of $F(c)$.

(2) When $e^{-mc^2/2kT}$ = 0 or, $c = \infty$, the expression is zero. This is also the minimal condition of $F(c)$.

(3) When $1 - \frac{mc^2}{2kT}$ = 0, the expression is again zero and it is the maximal condition of $F(c)$ and this c is c_{mp}.

Thus, $1 - \frac{mc_{mp}^2}{2kT}$ = 0 or, $c_{mp} = \sqrt{\frac{2kT}{m}}$ or, $c_{mp} = \sqrt{\frac{2RT}{M}}$. This is the expression of most-probable speed, c_{mp}.

Problem: Calculate most-probable speed, c_{mp} of oxygen gas molecules at 300 K temperature. **[Ans. 394.7 m/s]**

$F(c_{mp})$ is less at higher temperature

The fraction of molecules having c_{mp} is decreased with rise in T and this can be shown by diagram and also by mathematics. In the diagram as shown earlier, it is clear that $F(c_{mp})$ is decreased at higher T. Now we show it by mathematics.

$F(c)=4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT}c^2$. But when c = c_{mp}, then $F(c_{mp})=4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc_{mp}^2/2kT}c_{mp}^2$

Putting the value of $c_{mp}=\sqrt{\frac{2kT}{m}}$, we have $F(c_{mp})=4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-1}\left(\frac{2kT}{m}\right)$ or, $F(c_{mp})=4\left(\frac{m}{2\pi kT}\right)^{1/2}e^{-1}$

or, $F(c_{mp})=A'/\sqrt{T}$ or, $F(c_{mp})\propto 1/\sqrt{T}$. This shows that $F(c_{mp})$ decreases with rise in T for a given gas.

Problem: For an ideal gas obeying the Maxwellian distribution of molecular speeds in three-dimension, find the maximum value of $\left(\frac{1}{N}\right)\frac{dN}{dc}$ for a gas of molar mass 4.0 gm mol^{-1} kept at 127 ^{o}C.

[CU 2012, Q5 (a), m = 3]

Solution: When c = $c_{mp}=\sqrt{\frac{2kT}{m}}$, $\left(\frac{1}{N}\right)\frac{dN}{dc}$ attains maximum value and it is $4\times\left(\frac{M}{2\pi RT}\right)^{1/2}e^{-1}$ (See the above expression after proper simplifications). Putting the data given, we get maximum value of

$$\left(\frac{1}{N}\right)\frac{dN}{dc}=4\times\left(\frac{4.0\,gm\,mol^{-1}}{2\times3.14\times8.31\times10^{7}\,erg\,mol^{-1}K^{-1}\times400\,K}\right)^{1/2}e^{-1}=6.44\times10^{-6}\,(cm/\sec)^{-1}.$$

Expression of average speed ($\bar{c}$)

Using the process of averaging, we have $\bar{c}=\int_0^\infty c\times\frac{dn_c}{n}=\int_0^\infty c\times F(c)dc$

Inserting the expression of $F(c)$ and integrating, $\bar{c}=\int_0^\infty c\times4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-mc^2/2kT}c^2dc$

$$=4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty e^{-mc^2/2kT}c^3dc=4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\times\frac{\Gamma(2)}{2b^2}=4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\times\frac{1}{2}\left(\frac{2kT}{m}\right)^2=\sqrt{\frac{8kT}{\pi m}}.$$

Thus, the average speed of the molecules, $\bar{c}=\sqrt{\frac{8kT}{\pi m}}$ or, $\bar{c}=\sqrt{\frac{8RT}{\pi M}}$.

Problem: Calculate the average speed , $\bar{c}$ of oxygen molecules at 300 K temperature

Solution: $\bar{c}=\sqrt{\frac{8\times8.314\,J\,mol^{-1}K^{-1}\times300\,K}{3.14\times32\times10^{-3}\,kg\,mol^{-1}}}=445.5\,m/s$.

Expression of root-mean-square speed, $\sqrt{\overline{c^2}}$

Earlier we have calculated mean-square speed, $\overline{c^2}=\frac{3kT}{m}$.

Thus, root-mean-square speed, $\sqrt{\overline{c^2}}=\sqrt{\frac{3kT}{m}}$ or, $\sqrt{\overline{c^2}}=\sqrt{\frac{3RT}{M}}$.

Problem: Calculate the root-mean-square speed (c_{RMS}) of oxygen molecules at 300 K temperature.

Solution: $\sqrt{\overline{c^2}}=\sqrt{\frac{3\times8.314\,J\,mol^{-1}K^{-1}\times300\,K}{32\times10^{-3}\,kg\,mol^{-1}}}=483.4\,m/s$.

Thus it is seen that $c_{mp} < \bar{c} < \sqrt{\overline{c^2}}$. The ratio of the speeds are given as below

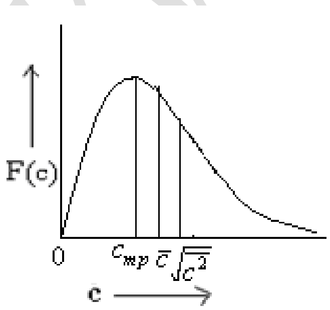
$$c_{mp} : \bar{c} : \sqrt{\overline{c^2}} = \sqrt{\frac{2kT}{m}} : \sqrt{\frac{8kT}{\pi m}} : \sqrt{\frac{3kT}{m}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1 : \sqrt{\frac{4}{\pi}} : \sqrt{\frac{3}{2}} = 1 : 1.13 : 1.22.$$

Problem: A hypothetical molecular speed distribution is $\frac{1}{N}\left(\frac{dn_c}{dc}\right) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT}$, where c goes from 0 to ∞. (i) Draw the function graphically taking $\frac{1}{N}\left(\frac{dn_c}{dc}\right)$ as y – axis and c as x- axis.

(ii) Calculate the average speed of the gas molecules using the above distribution.

[Calcutta Univ. 2010]

The position of these three speeds in the $F(c)$ vs. c curve are shown. The difference in the value of c_{mp} and $\bar{c}$ originates due to the fact that the distribution curve is not symmetrical. The peak of the curve is inclined towards the $F(c)$ -axis and hence c_{mp} has lower value. $\sqrt{\overline{c^2}}$ contains sum of square terms and this is why its value is highest.



Expression of standard deviation of molecular speeds, $\sqrt{\overline{\delta^2}}$

Since the speeds of the molecules are distributed**,** we can talk about the deviation of the speed of the molecule from the mean value**,** $\delta = c - \bar{c}$ **.** The average deviation from the mean value is zero. However, the root-mean-square deviation (which is called standard deviation of speed) $\sigma_c = \sqrt{\overline{\delta^2}}$ is non-zero. Let us now find the standard deviation of speed of the molecules in a gas assembly at a given temperature. We have discussed that in a given gas under steady-state, definite fraction of molecules has definite speeds. So, let n_1 molecule have speed c_1, n_2 molecules have speed c_2, n_3 molecules have speed c_3 and so on. Thus, deviation of speeds for n_1 molecules from its average value is $\delta_1 = c_1 - \bar{c}$, for n_2 molecules is $\delta_2 = c_2 - \bar{c}$, for n_3 molecules is $c_3 - \bar{c}$ and so.

Mean-square-deviation,

$$\overline{\delta^2} = \frac{n_1\,\delta_1^{\,2} + n_2\,\delta_2^{\,2} + n_3\,\delta_3^{\,2} + \ldots}{n} = \frac{n_1(c_1 - \bar{c})^2 + n_2(c_2 - \bar{c})^2 + n_3(c_3 - \bar{c})^2 + \ldots..}{n}$$

$$= \frac{n_1\left\{c_1^2 - 2c_1\bar{c} + (\bar{c})^2\right\} + n_2\left\{c_2^2 - 2c_2\bar{c} + (\bar{c})^2\right\} + n_3\left\{c_3^2 - 2c_3\bar{c} + (\bar{c})^2\right\} + \ldots.}{n}$$

$$= \frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \ldots}{n} - \frac{2\bar{c}\left(n_1c_1 + n_2c_2 + n_3c_3 + \ldots\right)}{n} + (\bar{c})^2\left\{\frac{n_1 + n_2 + n_3 + \ldots}{n}\right\} = \overline{c^2} - 2\left(\bar{c}\right)^2 + \left(\bar{c}\right)^2$$

or, $\overline{\delta^2} = \overline{c^2} - \left(\bar{c}\right)^2$ = (+ve). Thus $\overline{c^2} > \left(\bar{c}\right)^2$ or, $\sqrt{\overline{c^2}} > \bar{c}$.

This shows that RMS speed is greater than average speed of the molecules.

Putting the values of these speeds, we get $\overline{\delta^2} = \frac{3kT}{m} - \frac{8kT}{\pi m} = \frac{kT}{m}\left(3 - \frac{8}{\pi}\right)$, Thus root-mean-square deviation which is called standard deviation of speed is $\sigma_c = \sqrt{\overline{\delta^2}} = \sqrt{\frac{kT}{m}\left(3 - \frac{8}{\pi}\right)}$ or, $\sqrt{\overline{\delta^2}} = \sqrt{\frac{RT}{M}\left(3 - \frac{8}{\pi}\right)} = 0.67 \times \sqrt{\frac{RT}{M}}$.

This quantity gives us a measure of the breadth of the distribution.

Problem: Calculate the difference between RMS speed and average speed for an ideal gas exhibiting Maxwellian distribution of molecular speeds, given the molar mass is 2.0 gm mol^{-1}, density is 0.089 gm L^{-1} and the pressure is 1.0 atm. **[CU 2012, Q 1(a)]**

Solution: For ideal gas, $P = \frac{dRT}{M}$ or, $\frac{RT}{M} = \frac{P}{d}$. We have $c_{RMS} - \bar{c} = \sqrt{\frac{3RT}{M}} - \sqrt{\frac{8RT}{\pi M}}$

= $\left(\sqrt{3} - \sqrt{\frac{8}{\pi}}\right) \times \sqrt{\frac{RT}{M}}$ =. $0.136 \times \sqrt{\frac{RT}{M}} = 0.136 \times \sqrt{\frac{P}{d}}$. Putting the values, we have

$$c_{RMS} - \bar{c} = 0.136 \times \sqrt{\frac{1.0\, atm}{0.089\, gm\, L^{-1}}} = 0.136 \times \sqrt{\frac{76 \times 13.6 \times 981\, dyne\, cm^{-2}}{0.089\, gm \times 10^{-3} cm^{-3}}} = 14{,}516 \text{ cm/sec.}$$

problem: The standard deviation of speed (σ_c) for Maxwell's distribution satisfies the relation

(1) $\sigma_c \propto T$ (2) $\sigma_c \propto \sqrt{T}$ (3) $\sigma_c \propto 1/T$ (4) $\sigma_c \propto 1/\sqrt{T}$ **[NET (CSIR - UGC), 2013]**

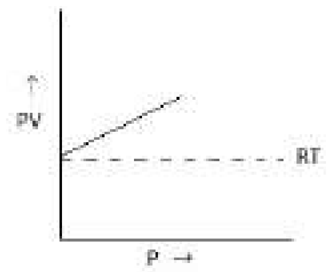
Expression of average time required to travel unit distance

Average value of any property can be done if that property is directly related with the speed of the molecules. Thus the time required to travel unit distance is directly related to the speed as $t = \frac{1}{c}$. So, the average value of t is $\bar{t} = \int_0^\infty \frac{1}{c} F(c)\, dc$

or, $\bar{t} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty e^{-mc^2/}$ … $\left(\frac{m}{\right)^{3/2}$ … $\frac{\Gamma(1)}{/2kT)} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \times \frac{1}{2} \times \frac{2kT}{m} = \sqrt{\frac{2m}{\pi kT}}$.

Thus, average time required … olecules, $\bar{t} = \sqrt{\frac{2m}{\pi kT}} = \sqrt{\frac{2M}{\pi RT}}$.

Problem: Calculate the aver … distance for O_2 gas at 27 ^oC . **[Ans. 2.86 × 10^{-3}s/m]**



Distribution of momentum

Any propert … speed can be made under distribution from Maxwell speed distribution law. Such properties are momentum and kinetic energy.

For momentum, $p = mc$, the speed c is now replaced by p in the speed distribution and we get the momentum distribution. The speed distribution is

$\frac{dn_c}{n} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} c^2 dc$. Now, $c = \frac{p}{m}$, $mc^2 = \frac{p^2}{m}$, $c^2 = \frac{p^2}{m^2}$ and $dc = \frac{dp}{m}$.

Putting these values, we have the Maxwell momentum distribution $\frac{dn_p}{n} = 4\pi\left(\frac{1}{2\pi mkT}\right)^{3/2} e^{-p^2/2mkT} p^2 dp$.

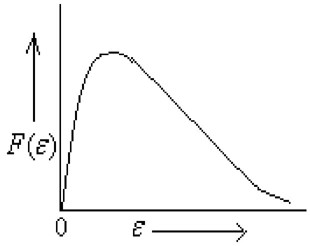
Distribution of kinetic energy of the gas molecules

This distribution is important one and this can also be done by replacing c by kinetic energy, ε using the relation, $\varepsilon = \frac{1}{2}mc^2$. Now, $c^2 = \frac{2\varepsilon}{m}$ so $2c\,dc = \frac{2}{m} d\varepsilon$

or, $dc = \frac{1}{mc} d\varepsilon = \frac{1}{m\sqrt{\frac{2\varepsilon}{m}}} d\varepsilon = \frac{1}{\sqrt{2m\varepsilon}} d\varepsilon$. Putting these values, we get the Maxwell KE distribution as

$$\frac{dn_\varepsilon}{n} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\varepsilon/kT} \left(\frac{2\varepsilon}{m}\right) \frac{1}{\sqrt{2m\varepsilon}} d\varepsilon \quad \text{or,} \quad \frac{dn_\varepsilon}{n} = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2} e^{-\varepsilon/kT} \sqrt{\varepsilon}\, d\varepsilon .$$

One important point of difference from the speed distribution is that it 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.
Thus, all gases have same KE distribution at a given T.



KE distribution function, $F(\varepsilon)=\frac{1}{n}\frac{dn_\varepsilon}{d\varepsilon}$ or, $F(\varepsilon)=2\pi\left(\frac{1}{\pi kT}\right)^{3/2}e^{-\varepsilon/kT}\sqrt{\varepsilon}$.

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

Expression of average KE of molecules

Average KE of molecules can be obtained by the process of averaging

$$\bar{\varepsilon}=\int_0^\infty \varepsilon\times\frac{dn_\varepsilon}{n}=2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\int_0^\infty \varepsilon^{3/2}\,e^{-\varepsilon/kT}d\varepsilon=2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\times\frac{\Gamma(5/2)}{(1/kT)^{5/2}}=2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\times\frac{3}{2}\times\frac{1}{2}\sqrt{\pi}\times(kT)^{5/2}$$

or, $\bar{\varepsilon}=\frac{3}{2}kT$. Thus, the expression of average KE shows that it depends on T only and does not depend on the nature of the gas. So, the most light gas H_2 and most heavy gas UF_6 both have the same average KE at a given temperature, i.e., $\bar{\varepsilon}_{H_2(g)}=\bar{\varepsilon}_{UF_6(g)}$.

Expression of fraction of molecules having KE $\geq\varepsilon_1$

The fraction of molecules having KE $\geq\varepsilon_1$ is calculated as below:

$\frac{n_{\varepsilon_1}}{n}=\int_{\varepsilon_1}^\infty\frac{dn_\varepsilon}{n}=2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\int_{\varepsilon_1}^\infty e^{-\varepsilon/kT}\sqrt{\varepsilon}\,d\varepsilon$. Let $\varepsilon=kT\,x^2$ so, $d\varepsilon=kT\;d\left(x^2\right)$,

When, $\varepsilon=\varepsilon_1$, $x=\sqrt{\varepsilon_1/kT}$ so, $\frac{n_{\varepsilon_1}}{n}=2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\int_{\sqrt{\varepsilon_1/kT}}^\infty e^{-x^2}\times\sqrt{kT}\,x\times kTd\left(x^2\right)=\frac{2}{\sqrt{\pi}}\int_{\sqrt{\varepsilon_1/kT}}^\infty x\,e^{-x^2}d\left(x^2\right)$

or, $$\frac{n_{\varepsilon_1}}{n}=-\frac{2}{\sqrt{\pi}}\int_{\sqrt{\varepsilon_1/kT}}^\infty x\,d\left(e^{-x^2}\right)=-\frac{2}{\sqrt{\pi}}\left[\left\{xe^{-x^2}\right\}_{\sqrt{\varepsilon_1/kT}}^\infty-\int_{\sqrt{\varepsilon_1/kT}}^\infty\left(e^{-x^2}\right)dx\right]=\frac{2}{\sqrt{\pi}}\sqrt{\frac{\varepsilon_1}{kT}}\,e^{-\varepsilon_1/kT}.$$

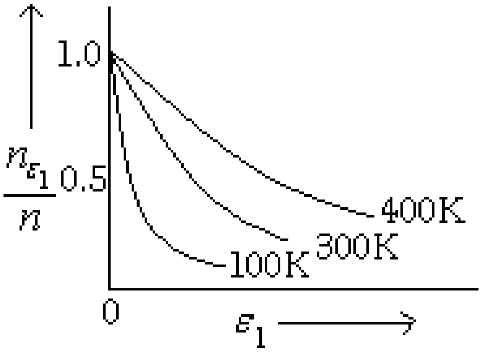
Generally, $\varepsilon_1>>kT$ so, $\frac{\varepsilon_1}{kT}$ is very large and $e^{-x^2}=e^{-\varepsilon_1/kT}$ is very small, and the second term is neglected.

So, the fraction of molecules having KE $\geq\varepsilon_1$ is $\frac{n_{\varepsilon_1}}{n}=\frac{2}{\sqrt{\pi}}\sqrt{\frac{\varepsilon_1}{kT}}\,e^{-\varepsilon_1/kT}$.

When KE is expressed per mole, ε_1 is replaced by E_1 and the fraction is $\frac{n_{E_1}}{n}=\frac{2}{\sqrt{\pi}}\sqrt{\frac{E_1}{RT}}\,e^{-E_1/RT}$.

RHS of the equation varies quite rapidly with temperature particularly at low temperatures.

The adjoining figure shows such variation of $\frac{n_{\varepsilon_1}}{n}$ with ε_1 at different temperatures, calculated by using the above expression. The figure also shows graphically that the fraction of molecules having KE $\geq \varepsilon_1$ increases markedly with rise in temperature, particularly if ε_1 is in the high energy range. This is fundamental especially in the domain of chemical reactions.



Problem: Calculate the % of oxygen molecules having KE $\geq$ 60 cal mol^{-1} at 27 $^{\circ}$C. **[Ans. 32.28 %]**

Maxwell distribution law in one dimension

The probability of a molecule that have x- component velocity u to $u+du$ is $P(u) = f(u)du$, but $P(u) = \frac{dn_u}{n}$ so, $\frac{dn_u}{n} = f(u)du$. The function is already evaluated and it is exponential in nature. The function contains u^2 and not u for the isotropic behavior of molecular motion. Thus, the function is $f(u) = A\,e^{-bu^2}$. Therefore, $\frac{dn_u}{n} = A\,e^{-bu^2}\,du$. The value of A can be obtained from the normalization condition of the function, $\int_{-\infty}^{+\infty} f(u)du = 1$ so, $A\int_{-\infty}^{+\infty} e^{-bu^2}\,du = 1$ or, $2A\int_{0}^{+\infty} e^{-bu^2}\,du = 1$

or, $2A\times\frac{1}{2}\frac{\Gamma(1/2)}{b^{1/2}} = 1$ or, $A\sqrt{\frac{\pi}{b}} = 1$ or, $A = \sqrt{\frac{b}{\pi}}$. The distribution is thus $\frac{dn_u}{n} = \sqrt{\frac{b}{\pi}}\,e^{-bu^2}\,du$.

Now evaluation of b can be done from the value of mean-square x- component velocity from the distribution equation and equated with the value obtained from kinetic theory of gas.

$$\overline{u^2} = \int_{-\infty}^{+\infty} u^2\, f(u)du = A\int_{-\infty}^{+\infty} u^2\, e^{-bu^2}\,du = 2A\int_{0}^{+\infty} u^2\, e^{-bu^2}\,du = 2\sqrt{\frac{b}{\pi}}\times\frac{1}{2}\frac{\Gamma(3/2)}{b^{3/2}} = \sqrt{\frac{b}{\pi}}\times\frac{1}{b^{3/2}}\times\frac{1}{2}\sqrt{\pi} = \frac{1}{2b}.$$

But from kinetic theory, $\overline{\varepsilon_x} = \frac{1}{2}m\overline{u^2} = \frac{1}{2}kT$ or, $\overline{u^2} = \frac{kT}{m}$ so, $\frac{1}{2b} = \frac{kT}{m}$ or, $b = \frac{m}{2kT}$.

Thus, Maxwell distribution law in one dimension is $\frac{dn_u}{n} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu^2/2kT}\,du$.

Expression of average value of x- component velocity, $(\bar{u})$

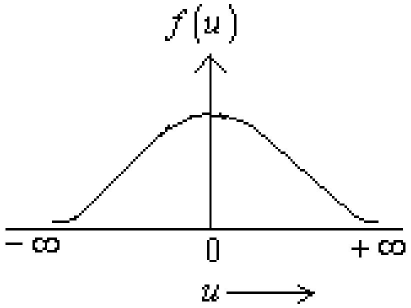
$\bar{u} = \int_{-\infty}^{+\infty} u\, f(u)du = A\int_{-\infty}^{+\infty} u\, e^{-bu^2}\,du = 0$. [Since, $\int_{-\infty}^{+\infty} u\, e^{-bu^2}\,du = 0$.] This result is due to the fact that a molecule is equally likely to be moving in a (+ve) direction as in a (-ve) direction. If $\bar{u}$ had a value other than zero, this would correspond to a net motion of the entire mass of gas in that particular direction.

Graphical representation of x-component velocity function, $f(u)$

The above function is $f(u) = \frac{1}{n}\frac{dn_u}{du} = Ae^{-bu^2}$.

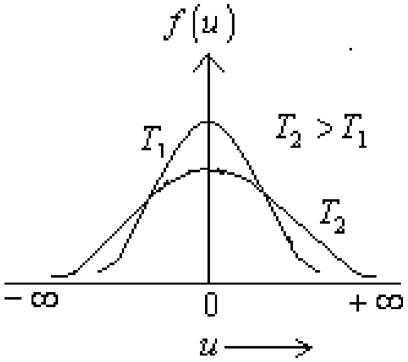
The distribution function, $f(u)$ when plotted against u of a gas at a given T, the curve becomes symmetrical and average x-component velocity, $\bar{u}$ = 0.

Again, the function, $f(u)$ attains maximum value when u = 0



so, the most-probable x-component velocity, $u_{mp} = 0$.

When T is increased, the curve becomes more flat and the distribution is more uniform. The peak of the curve is lower but it is broadened. However, the area of each curve is unity.



Expression of root-mean-square of x - component velocity

We have already formulated mean-square x-component velocity using the process of averaging from the distribution law in one- dimensional motion as $\overline{u^2} = \frac{kT}{m}$. So, the root-mean-square velocity, $\sqrt{\overline{u^2}} = \sqrt{\frac{kT}{m}}$ or, $\sqrt{\overline{u^2}} = \sqrt{\frac{RT}{M}}$. Comparison of different average x-component velocities are: $\bar{u} = u_{mp} = 0$ and $\sqrt{\overline{u^2}} = \sqrt{\frac{}{m}}$. In $\sqrt{\overline{u^2}}$, each velocity term (u) is squared up so it becomes (+ve).

Question: Show that total probability of a molecule to have velocity u to $u + du$ within the range $-\infty$ to $+\infty$ is unity.

Answer: $$\int\limits_{all\ values\ of\ u} P(u) = \int_{-\infty}^{+\infty} f(u)\,du = \int_{-\infty}^{+\infty} A\ e^{-bu^2}\ du = 2A\int_{0}^{+\infty} e^{-bu^2}\ du = 2\sqrt{\frac{b}{\pi}} \times \frac{1}{2} \times \frac{\Gamma(1/2)}{b^{1/2}} = \sqrt{\frac{b}{\pi}} \times \sqrt{\frac{\pi}{b}} = 1.$$

Expression of average x - component velocity in the range 0 to $+\infty$

When all the molecules are moving in one direction only, the expression of the function, $f(u) = 2A\,e^{-bu^2}$.

This expression can be easily obtained from the normalization condition, $\int_0^{+\infty} f(u)\,du = 1$.

Thus, the average value of x-component velocity in the range 0 to $+\infty$ is calculated as below (All the molecules are moving in one direction so it is multiplied by 2):

$$\bar{u} = \int_0^{+\infty} u\ f(u)\,du = 2A\int_0^{+\infty} u\ e^{-bu^2}\ du = 2A \times \frac{1}{2b} = \sqrt{\frac{b}{\pi}} \times \frac{1}{b} = \frac{1}{\sqrt{b\pi}} = \sqrt{\frac{2kT}{\pi m}} \quad \text{or, } \bar{u} = \sqrt{\frac{2RT}{\pi M}}.$$

Problem:

A sample of caesium is heated to 500 °C in an oven. In one wall, there is a small hole and the atoms emerge to form an atomic beam. Find the average velocity of the atomic beam.

Solution: $$\bar{u} = \sqrt{\frac{2RT}{\pi M}} = \sqrt{\frac{2 \times 8.314\,J\ mol^{-1}K^{-1} \times (273+500)\,K}{3.14 \times 133 \times 10^{-3}\,kg\ mol^{-1}}} = 175.5\,m\,s^{-1}.$$

KE distribution in one dimension

Maxwell x-component velocity distribution is $\frac{dn_u}{n} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu^2/2kT} du$. Now, $\varepsilon_x = \frac{1}{2}mu^2$

so, $d\varepsilon_x = mu\,du = m \times \sqrt{\frac{2\varepsilon_x}{m}}\ du = \sqrt{2m\varepsilon_x}\ du$ or, $du = \frac{1}{\sqrt{2m\varepsilon_x}} d\varepsilon_x$. Replacing u by ε_x, we get the distribution in one dimension, $\frac{dn_{\varepsilon_x}}{n} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\varepsilon_x/kT} \times \frac{1}{\sqrt{2m\varepsilon_x}} d\varepsilon_x = \frac{1}{2}\left(\frac{1}{\pi kT}\right)^{1/2} e^{-\varepsilon_x/kT} \times \frac{1}{\sqrt{\varepsilon_x}}\ d\varepsilon_x$.

Thus, KE distribution law in one dimension is $$\frac{dn_{\varepsilon_x}}{n} = \frac{1}{2}\left(\frac{1}{\pi kT}\right)^{1/2} e^{-\varepsilon_x/kT} \times \frac{1}{\sqrt{\varepsilon_x}}\ d\varepsilon_x.$$

This KE distribution is also independent of molecular mass (m) of the gas but dependent of T.

Expression of average KE of molecules in one dimensional motion

$$\overline{\varepsilon_x} = \int_0^\infty \varepsilon_x \frac{dn_{\varepsilon_x}}{n} = 2\int_0^\infty \varepsilon_x \times \frac{1}{2}\left(\frac{1}{\pi kT}\right)^{1/2} e^{-\varepsilon_x/kT} \times \frac{1}{\sqrt{\varepsilon_x}}\, d\varepsilon_x \quad \text{[Since the molecules move in one direction only]}$$

$$= \left(\frac{1}{\pi kT}\right)^{1/2} \int_0^\infty \sqrt{\varepsilon_x} \times e^{-\varepsilon_x/kT} d\varepsilon_x = \left(\frac{1}{\pi kT}\right)^{1/2} \times \frac{\Gamma(3/2)}{\left(1/kT\right)^{3/2}} = \left(\frac{1}{\pi kT}\right)^{1/2} \times (kT)^{3/2} \times \frac{1}{2}\sqrt{\pi} = \frac{1}{2}kT\ .$$

This average value can also be calculated from mean-square x - component velocity by the relation,

$$\overline{\varepsilon_x} = \frac{1}{2} m\, \overline{u^2} = \frac{1}{2} m \int_{-\infty}^{+\infty} u^2 \frac{dn_u}{n} = \frac{1}{2}kT\ .$$

Speed distribution law in planar motion (2-D motion)

The molecules in this type of motion have both x - component and y -component velocities simultaneously. Thus, the probability of a molecule that has velocity u to $u+du$ and v to $v+dv$ simultaneously is

$$P(uv) = P(u) \times P(v) = f(u)\,du \times f(v)\,dv = f(u)\,f(v)\,du\,dv\,.$$

But, $P(uv) = \frac{dn_{uv}}{n}$, so the fraction of molecules that have velocity u and v simultaneously within range du and dv is $\frac{dn_{uv}}{n} = f(u)\,f(v)\,du\,dv = Ae^{-bu^2} \times Ae^{-bv^2} du\,dv = A^2 e^{-b(u^2+v^2)} du\,dv = A^2 e^{-bc^2} du\,dv$.

But, $A = \sqrt{\frac{b}{\pi}}$ and $b = \frac{m}{2kT}$, putting the values, we get $\frac{dn_{uv}}{n} = \left(\frac{m}{2\pi kT}\right) e^{-mc^2/2kT} du\,dv$.

Converting the distribution in polar co-ordinates, we have $\frac{dn_{c\varphi}}{n} = \left(\frac{m}{2\pi kT}\right) e^{-mc^2/2kT} c\,dc\,d\varphi$.

When only speeds are considered, $d\varphi$ is to be integrated within full limits and it is

$\frac{dn_c}{n} = \left(\frac{m}{2\pi kT}\right) e^{-mc^2/2kT} c\,dc \int_0^{2\pi} d\varphi$ or, $\frac{dn_c}{n} = \left(\frac{m}{kT}\right) e^{-mc^2/2kT} c\,dc$ Thus, Maxwell speed distribution law of molecules for planar motion is $F(c) = \frac{1}{n}\frac{dn_c}{dc}$, so the distribution function $F(c) = \left(\frac{m}{kT}\right) e^{-mc^2/2kT} c$.

The curve, $F(c)$ vs. c rises more gently but falls more rapidly than the curve in three dimensional motion.

Expression of most-probable speed of molecules in planar motion

Differentiating the speed distribution function, $F(c)$ with respect to c, we have

$$\frac{dF(c)}{dc} = \left(\frac{m}{kT}\right)\left[e^{-mc^2/2kT} + c\, e^{-mc^2/2kT}\left(-\frac{2mc}{2kT}\right)\right] = \left(\frac{m}{kT}\right) e^{-mc^2/2kT}\left(1 - \frac{mc^2}{kT}\right) = 0\,.$$

When $e^{-mc^2/2kT} = 0$, $c \to \infty$ and this corresponds minimal value of c and $1 - \frac{mc^2}{kT} = 0$ corresponds to the maximal value of c. Thus, $1 - \frac{mc_{mp}^2}{kT} = 0$ so, the most-probable speed $c_{mp} = \sqrt{\frac{kT}{m}}$ or, $c_{mp} = \sqrt{\frac{RT}{M}}$.

Expression of average speed of molecules in planar motion

We have distribution function, $F(c)=\left(\frac{m}{kT}\right)e^{-mc^2/2kT}c$. So the average speed,

$$\bar{c}=\int_0^\infty c\times F(c)\,dc=\int_0^\infty c\times\left(\frac{m}{kT}\right)e^{-mc^2/2kT}c\,dc=\left(\frac{m}{kT}\right)\int_0^\infty c^2\times e^{-mc^2/2kT}\,dc=\left(\frac{m}{kT}\right)\times\frac{\Gamma(3/2)}{2\left(m/2kT\right)^{3/2}}$$

$$=\left(\frac{m}{kT}\right)\times\frac{\sqrt{\pi}}{4}\times\left(\frac{2kT}{m}\right)^{3/2}=\sqrt{\frac{\pi kT}{2m}}\ \text{ so, }\ \bar{c}=\sqrt{\frac{\pi kT}{2m}}=\sqrt{\frac{\pi RT}{2M}}\,.$$

Expression of root-mean-square speed of molecules in planar motion

This expression can be formulated from the distribution law, $F(c)=\left(\frac{m}{kT}\right)e^{-mc^2/2kT}c$.

The mean-square speed,

$$\overline{c^2}=\int_0^\infty c^2\times F(c)\,dc=\int_0^\infty c^2\times\left(\frac{m}{kT}\right)e^{-mc^2/2kT}c\,dc=\left(\frac{m}{kT}\right)\int_0^\infty c^3\times e^{-mc^2/2kT}\,dc=\left(\frac{m}{kT}\right)\times\frac{\Gamma(2)}{2\left(m/2kT\right)^2}$$

$$=\left(\frac{m}{kT}\right)\times\frac{1}{2}\times\left(\frac{2kT}{m}\right)^2=\frac{2kT}{m}\text{. So, RMS speed, }\sqrt{\overline{c^2}}=\sqrt{\frac{2kT}{m}}=\sqrt{\frac{2RT}{M}}\,.$$

Thus, the comparison of different average speeds are made from the above expressions

$$c_{mp}:\bar{c}:\sqrt{\overline{c^2}}=\sqrt{\frac{kT}{m}}:\sqrt{\frac{\pi kT}{2m}}:\sqrt{\frac{2kT}{m}}=1:\sqrt{\frac{\pi}{2}}:\sqrt{2}=1:1.253:1.414\,.$$

KE distribution of molecules in planar motion

The KE, $\varepsilon=\frac{1}{2}mc^2$ so, $d\varepsilon=m\,cdc$. Putting in the speed distribution law, we get the KE distribution equation. $\frac{dn_\varepsilon}{n}=\left(\frac{m}{kT}\right)e^{-\varepsilon/kT}\frac{d\varepsilon}{m}$ or, $\frac{dn_\varepsilon}{n}=\left(\frac{1}{kT}\right)e^{-\varepsilon/kT}d\varepsilon$.

Thus, KE distribution is independent of molecular mass but it depends only on T.

Fraction of molecules having KE $\geq\varepsilon_1$ in the planar motion

$$\frac{n_{\varepsilon_1}}{n}=\left(\frac{1}{kT}\right)\int_{\varepsilon_1}^\infty e^{-\varepsilon/kT}d\varepsilon=\left(\frac{1}{kT}\right)\times\left[-\frac{e^{-\varepsilon/kT}}{1/kT}\right]_{\varepsilon_1}^\infty=e^{-\varepsilon_1/kT}$$

Thus, fraction of molecules having KE $\geq\varepsilon_1$ is

$$\frac{n_{\varepsilon_1}}{n}=e^{-\varepsilon_1/kT}\text{. When KE is expressed per mole (E}_1\text{), it is }\ \frac{dn_{E_1}}{n}=e^{-E_1/RT}\,.$$

Problem: Calculate % of oxygen molecules having KE $\geq$ 60 cal mole^{-1} at 27 ^{o}C. **[Ans. 90. 5]**

Principle of equipartition of energy

The principle is based on classical theory and it is much helpful to calculate average energy ($\bar{\varepsilon}$) of a molecule and also molar heat capacities of the gas.

Statement of the principle

If the energy of a molecule can be expressed as sum of terms, each of which is proportional to either square of velocity component or square of position, then each of the square term contributes $\frac{1}{2}kT$ *to the average value.*

Verification of the principle:

Maxwell velocity distribution law can be used to justify this principle from the value of x - component translational KE ($\bar{\varepsilon}_x$) that contains square of velocity (u) term.

$\bar{\varepsilon}_x = \frac{1}{2}m\,\overline{u^2} = \frac{1}{2}m\int_{-\infty}^{+\infty} u^2 f(u)\,du$, but $f(u) = A\,e^{-bu^2}$, where $A = \sqrt{\frac{b}{\pi}}$ and $b = \frac{m}{2kT}$

$$= \frac{1}{2}m \times 2A\int_{0}^{\infty} u^2 e^{-bu^2}\,du = m\sqrt{\frac{b}{\pi}} \times \frac{\Gamma(3/2)}{2b^{3/2}} = \frac{1}{2}m \times \frac{1}{\sqrt{\pi}} \times \frac{1}{b} \times \frac{1}{2}\sqrt{\pi} = \frac{1}{4}m \times \frac{2kT}{m} = \frac{1}{2}kT\ .$$

This shows that the square of x - component velocity term will add $\frac{1}{2}kT$ value.

Molecular motion

A molecule can execute three types of motions – translational, rotational and vibrational. The latter two constitute internal motion while former one is external motion.

Translational motion can be executed by a molecule in three independent axes (three degrees of freedom). So,

$$\bar{\varepsilon}_{trns} = \bar{\varepsilon}_x + \bar{\varepsilon}_y + \bar{\varepsilon}_z = \frac{1}{2}m\overline{u^2} + \frac{1}{2}m\overline{v^2} + \frac{1}{2}m\overline{w^2} = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT \quad \text{or,} \quad \bar{\varepsilon}_{trns} = \frac{3}{2}kT\ .$$

Rotational motion: A linear molecule can rotate in two axes independently. If bond axis is taken as x - axis, the molecule can rotate along y - axis and z - axis independently with centre of mass is at the origin. When it rotates along x - axis, there is no positional change of the molecule in space so, it is not counted. Thus,

$\bar{\varepsilon}_{rot} = \frac{1}{2}I\,\overline{\omega_y}^2 + \frac{1}{2}I\,\overline{\omega_z}^2 = \frac{1}{2}kT + \frac{1}{2}kT = kT$, where I = moment of inertia = μr^2 and ω_y and ω_z are the angular velocities of the molecule along y - axis and z - axis respectively so, for linear molecule, $\bar{\varepsilon}_{rot} = kT$.

Non-linear molecule can rotate along the three axes independently and so rotational KE,

$\bar{\varepsilon}_{rot} = \frac{1}{2}I\,\overline{\omega_x}^2 + \frac{1}{2}I\,\overline{\omega_y}^2 + \frac{1}{2}I\,\overline{\omega_z}^2 = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$. So for non-linear molecule, $\bar{\varepsilon}_{rot} = \frac{3}{2}kT$.

Vibrational motion: For each mode of vibration (say along x - axis) $\bar{\varepsilon}_{vib} = \frac{1}{2}m\overline{u^2} + \frac{1}{2}k\,x^2 = \frac{1}{2}kT + \frac{1}{2}kT = kT$.

It means that each mode of vibrational energy consists of two square terms so it posses energy, kT .

Degrees of freedom

The degrees of freedom of a particle may be defined as the number of co-ordinates necessary to describe the position of the particle in space.

Thus, for an atom, 3 co-ordinates are required to specify its position. So for a system containing N atoms, there requires 3N co-ordinates or degrees of freedom. Even when these atoms are in motion, still then 3N independent degrees of freedom are required to define the system.

If, however, the atoms are connected by covalent bonds, a molecule is formed but total degrees of freedom (3N) remain conserved.

Out of 3N degrees of freedom, the molecule execute 3 degrees of translational motion, 2 degrees of rotational motion (for linear molecule) and (3N – 5) degrees of vibrational motion.

Thus, for a linear molecule containing N atoms, we have total 3 +2 + (3N – 5) degrees of freedom.
Since each degree of vibrational energy constitutes two square terms, so a linear molecule has total
3 +2 + 2(3N – 5) square terms in its energy value.
For non-linear molecule, it has 3 +3 + 2(3N – 6) square terms.

Calculation of average energy of a molecule

The principle is used to find the average energy of a molecule. For a linear molecule consisting of N atoms, the average energy

$$\bar{\varepsilon} = \bar{\varepsilon}_{tran} + \bar{\varepsilon}_{rot} + \bar{\varepsilon}_{vib} = \left[3+2+2\left(3N-5\right)\right]\times\frac{1}{2}kT \; .$$

Thus, for CO_2 which is triatomic and linear, the average energy of the molecule in gaseous state is

$$\bar{\varepsilon} = \left[3+2+2\left(3\times3-5\right)\right]\times\frac{1}{2}kT = \frac{13}{2}kT = 6.5\,kT \; .$$

The average energy per mole is, $\bar{E} = 6.5RT$ and for n moles it is $E = 6.5nRT$.
So for 1 mole CO_2 gas at 27 °C, the average energy can be calculated as

$$\bar{E} = 6.5RT = 6.5\times2\;cal\;mol^{-1}K^{-1}\times300\;K = 3.9\times10^{3}\,cal\;mol^{-1} \, .$$

For a non-linear molecule consisting of N atoms, the average energy

$$\bar{\varepsilon} = \bar{\varepsilon}_{tran} + \bar{\varepsilon}_{rot} + \bar{\varepsilon}_{vib} = \left[3+3+2\left(3N-6\right)\right]\times\frac{1}{2}kT \; .$$

Thus, for H_2O which is triatomic and non-linear, the average energy of the molecule in gaseous state is

$$\bar{\varepsilon} = \left[3+3+2\left(3\times3-6\right)\right]\times\frac{1}{2}kT = 6\,kT \; .$$

The average energy per mole of H_2O gas is, $\bar{E} = 6\,RT$ and at 27 °C,

$$\bar{E} = 6\times2\;cal\;mol^{-1}K^{-1}\times300\;K = 3.6\times10^{3}\,cal\;mol^{-1} .$$

For monatomic gas like He, Ne, Ar etc, the molecule has only translational KE and no rotational and vibrational energy are there. So, the average energy of these molecules is

$\bar{\varepsilon} = \bar{\varepsilon}_{tran} = \frac{3}{2}kT$ and per mole, $\bar{E} = \frac{3}{2}RT$ and at 27 °C, $\bar{E} = \frac{3}{2}\times2\;cal\;mol^{-1}K^{-1}\times300\;K = 9\times10^{2}\,cal\;mol^{-1}$.

Molar heat capacity

This energy constitutes the translational, rotational and vibrational energy of the molecules, hence it is the internal energy of the system (U). The constant-volume molar heat capacity, $C_V = \left(\partial U/\partial T\right)_V$

and thus, $C_V = \left[3+2+2\left(3N-5\right)\right]\times\frac{1}{2}R$ for the gas constituting linear molecules.

and $C_V = \left[3+3+2\left(3N-6\right)\right]\times\frac{1}{2}R$ for the gas constituting non-linear molecules.

For monatomic gas, (N = 1) there is no rotational and vibrational motion so these motions do not contribute to the energy. Thus, $C_V = \frac{3}{2}R$ and $C_P = \frac{5}{2}R$, and molar heat capacity ratio $\gamma = C_P/C_V = 5/3 = 1.66$.
This shows that for monatomic gas, there is excellent matching with the experimental value of γ .

For diatomic gas, $U = \frac{7}{2}RT$ so, $C_V = \frac{7}{2}R$, $C_P = \frac{9}{2}R$ and $\gamma = \frac{9}{7} = 1.3$.
But the experimental value is 1.4 when determined at ordinary temperature
This discrepancy is much more pronounced for more complex molecules (for higher value of N).
The limitation originates due to the fact that the principle is derived from classical theory in which energy changes continuously. There occurs no limitation for monatomic gas in which translational energy changes continuously.

For polyatomic molecules, if contribution from the vibrational motion is not considered, then calculated value matches the experimental value. As for diatomic gas, it is then C_V = (5/2)R, C_P = (7/2)R and γ = 7/5 = 1.4 which matches excellently with the experimental value.

Limitations:

(1) C_V value is found from the law is independent of temperature (T), but C_V increases with increase of T. Thus when T decreases, C_V decreases and when $T \to 0K$, $C_V \to 0$ (Experimentally found).

$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1.4$ when determined at ordinary temperature. But as temperature is increased, the vibrational energy begins to contribute to the value of C_V and C_V is increased so γ of the gas is decreased. At high temperature, thus the value of γ from the law attains the experimental value.

Problem: According to equipartition principle, predicted at high temperature limiting value of the molar heat capacity at constant volume for C_2H_2 is

(A) $5.5R$ (B) $6.0R$ (C) $9.0R$ (D) $9.5R$. **[NET(CSIR – UGC) 2015, Calcutta Univ. 2015]**

Collision of gas molecules

The molecules are moving at random in all directions with equal probability in a gas. So, when a gas is confined within a vessel at equilibrium, there occurs collisions of the molecules with the walls of the vessel (called wall-collisions) and with themselves (called intermolecular collisions). By frequency of collisions, we mean the number of collisions made by the molecules in unit time.

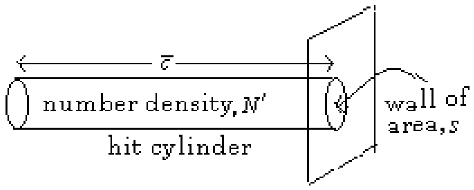
Frequency of wall-collisions (Z_w)

It is the number of collisions made by the molecules per unit area of the wall in unit time. The value of the Z_w can be estimated roughly or can be formulated accurately by using Maxwell one-dimensional velocity distribution. These are given as follows.

Approximate estimation

Let us consider a wall of area, s and the molecules that can hit the wall in unit time must be $\bar{c}$ distance away from the wall. $\bar{c}$ is the distance that the molecules can travel on an average in unit time. So the volume of the hit cylinder is $\bar{c} \times s$.

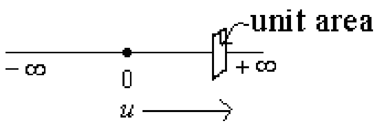
If N' is the number density of the molecules in the gas at temperature T and pressure P, then this cylinder contains $\bar{c} \times s \times N'$ number of molecules. Since the molecular motion is isotropic in nature, so only (1/6) of the above molecules can strike the wall of area s in unit time.



Thus the number of molecules that can collide unit area of a wall in unit time is $(Z_w) = \frac{1}{6} \bar{c} N'$.

Accurate expression using Maxwell one-dimension velocity distribution

Let us consider a gas at temperature T and pressure P containing N' molecules per unit volume (i.e., N' = N/V). Now let us take a wall of unit area placed perpendicular to the x- axis in the range 0 to $+\infty$. So, the molecules that hit this wall in unit time must have velocity u within the range 0 to $+\infty$. The molecules having velocity u within range 0 to $-\infty$ are moving in the wrong direction and they can never hit the wall of our reference.



The molecules that hit the wall in unit time must be u distance away from the wall. Since the wall is of unit area, these molecules must be contained within the volume ($u \times 1$).

Let dN'_u is the number of molecules per unit volume out of number density N' that have velocity u within range 0 to $+\infty$.

Thus the number of molecules hitting the unit area of the wall in unit time, which is frequency of wall-collision, is $Z_w = \int_0^\infty (u \times 1)\, dN'_u$. But, $dN'_u = N' A e^{-bu^2} du$, where $A = \sqrt{\frac{b}{\pi}}$ and $b = \frac{m}{2kT}$.

So, $Z_w = N' A \int_0^\infty u\, e^{-bu^2} du = N' \sqrt{\frac{b}{\pi}} \times \frac{1}{2b} = N' \times \sqrt{\frac{1}{4\pi b}} = \frac{1}{4} \times 4 N' \times \sqrt{\frac{2kT}{4\pi m}} = \frac{1}{4} \times N' \sqrt{\frac{8kT}{\pi m}} = \frac{1}{4} \times N' \bar{c}$

Thus, the frequency of wall-collision, $Z_w = \frac{1}{4} N' \bar{c}$.

The mass of the gas that strikes unit area in unit time, $\mu = Z_w \times m = \frac{1}{4}(N' \times m)\, \bar{c} = \frac{1}{4} d\, \bar{c}$,

(since $N' \times m = d$, density of the gas).

For ideal gas, $d = \frac{P \times M}{RT}$ and $\bar{c} = \sqrt{\frac{8RT}{\pi M}}$ so, $\mu = \frac{1}{4} \times \left(\frac{P \times M}{RT}\right) \times \left(\frac{8RT}{\pi M}\right) = P\sqrt{\frac{M}{2\pi RT}}$. Thus, $\mu = P\sqrt{\frac{M}{2\pi RT}}$.

This relation is used to determine vapour pressure of solid by Knudsen method. This determination is illustrated by the problem (4) as given below:

Questions:

(1) Using the appropriate form of Maxwell's distribution function in 1-D, arrive at following expression for the collision flux (Z_w) in the case of wall-molecule collision in 3-D, $Z_w = \frac{1}{4}\left({}^{N}\!/\!{}_{V}\right)\langle c\rangle$ collisions/area/time. Where $\left({}^{N}\!/\!{}_{V}\right)$ presents the number of molecules per unit volume of the gas under experimental conditions and $\langle c\rangle$ represents the average speed in 3-D of the gas. **[CU 2007, Q 1(d), m = 4]**

(2) Calculate the number of wall-molecule collisions per cm^2 per sec in O_2 gas at 25 ^oC and 1 atm pressure.
[**Ans.** 12.74 × 10^{23} collisions per cm^2 per sec] **[CU 2010, Q 1(b), m = 2]**

(3) The average speed of H_2 molecules is 2×10^5 cm/sec at t ^oC. Calculate the number of grams of H_2 per sec hitting 1 cm^2 of wall, if pressure of the gas is such that the molar volume is one litre.[**Ans.**100 gm cm^{-2} sec^{-1}]

(4) The vapour pressure of solid Be was measured using a Knudsen cell. The effusion hole was 0.318 cm in diameter and there occurred a weight loss of 9.54 mg in 60.1 minutes at a temperature of 1457 K. What is the vapour pressure of Be.

Ans. to Question (4): We have $\mu = P\sqrt{\frac{M}{2\pi RT}}$ or, $P = \mu \times \sqrt{\frac{2\pi RT}{M}}$. Putting the values, we get

$$P = \frac{9.54 \times 10^{-3}}{60.1 \times 60 \times 3.14 \times (0.159)^2}\ gm\ cm^{-2}\ \sec^{-1} \times \sqrt{\frac{2 \times 3.14 \times 8.314 \times 10^7 \times 1457\ K}{9.01}}\ \ cm\ \sec^{-1}$$

$$= 9.586\ dyne\ cm^{-2} = 9.45 \times 10^{-6}\ atm.$$

Graham's law of effusion

This law can be formulated from the expression of μ. The mass of the gas hitting a hole of area ds will be effused from the vessel.

Thus, $\frac{dw}{dt}$ = mass of the gas effusing in unit time through the hole = $\mu \times ds = \frac{1}{4}\rho \bar{c}\ ds$.

Again, $w = \rho \times v$ or, $\frac{dw}{dt} = \rho \times \frac{dv}{dt}$. But, $\frac{dv}{dt} = r_e$, rate of effusion of the gas.

Thus, $\rho \times r_e = \frac{1}{4}\rho \bar{c}\, ds$ or, $r_e = \frac{1}{4}\bar{c}\, ds$. But, $\bar{c} = \sqrt{\frac{8kT}{\pi m}}$ so, $r_e = \left(\frac{1}{4}\sqrt{\frac{8RT}{\pi}}\, ds\right) \times \frac{1}{\sqrt{M}}$

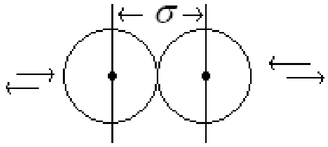
or, $r_e \propto \frac{1}{\sqrt{M}}$ for gas effusing from a vessel of definite hole area at constant temperature T .

This is Graham's law of effusion.

Question: How many times does the rate of effusion of a gas through a pin-hole into vacuum change when pressure is doubled and temperature is increased four times? (Ans. 2 times) **[CU 2011, Q 3(b), m = 2]**

Intermolecular collisions

As the molecules are in random motion so they collide with themselves also. The molecules are assumed as rigid spheres, so when the molecules collide, the centre of two molecules can not approach beyond a certain distance. This distance is called distance of closest approach or collision diameter (σ) of the molecules**.**

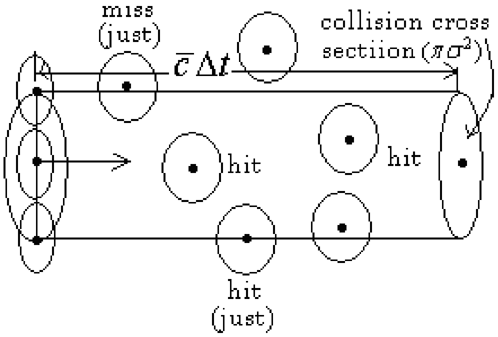


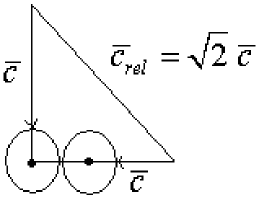
Expression of collision number of a molecule in unit time

Let us find an expression of the number of collisions made by a single molecule in unit time in a gas at temperature T and pressure P.

We count hit whenever the distance (r) between centre of two molecules is equal to or less than the collision diameter, i.e., $r \le \sigma$ and we call it a binary collision. The simplest approach to the problem is to freeze the position of all the molecules in space except one of our interest which is moving through the gas with an average speed $\bar{c}$. In doing so, it swept out a collision tube of area $\pi\sigma^2$ and length $\bar{c} \times \Delta t$ in time Δt .

This $\pi\sigma^2$ is also called collision cross section. The volume of the collision tube is $\pi\sigma^2\, \bar{c}\Delta t$. The molecules with centres inside this volume is $\pi\sigma^2\, \bar{c}\Delta t \times N'$, where N' is the number of molecules per unit volume (also called number density) of the gas. All these molecules whose centres are within this volume are suffered collisions by the moving molecule in Δt time. So, the number of collisions made by the mobile molecule in unit time is $Z_1 = \pi\sigma^2\, \bar{c}\, N'$.





But we have taken a wrong supposition that only one molecule is moving with average speed, $\bar{c}$ and other molecules are at rest. To rectify this, we have to use average relative speed ($\bar{c}_{rel}$) of the colliding molecule.

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That is, if all the molecules are moving with average speed, $\bar{c}$ then the mobile molecule of our interest is moving with $\bar{c}_{rel}$ which is $\sqrt{2}\,\bar{c}$. Thus, the expression of number of collisions made by a single molecule in unit time is

$$Z_1 = \sqrt{2}\,\pi\sigma^2\, \bar{c}\, N'$$

Mean-free path (λ)

The distance between two successive collisions of a molecule is called free path. The free path of a molecule can range for 0 to ∞ as a molecule can collide with the other molecule just immediately after the start of its motion or it can move long distance without suffering any collision. This is why, we talk of mean-free path (λ) and it is defined as the average distance traveled by a molecule between two successive collisions and it is formulated as, $\lambda = \dfrac{\bar{c}}{Z_1}$, where Z_1 is the number of collisions made by a molecule in unit time when it travels $\bar{c}$ distance. Putting the value of Z_1, we get the expression of mean-free path, $\lambda = \dfrac{\bar{c}}{\sqrt{2}\,\pi\sigma^2\,\bar{c}\,N'}$ or, $\lambda = \dfrac{1}{\sqrt{2}\,\pi\sigma^2\,N'}$.

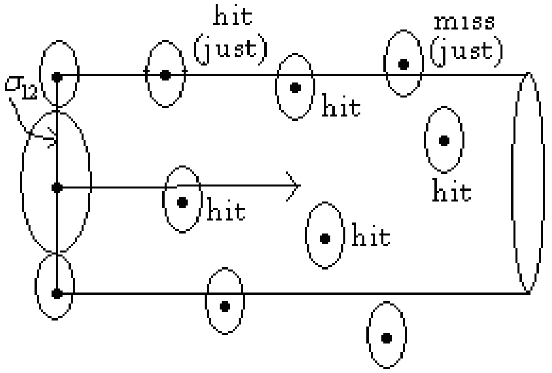
Frequency of binary collisions among the same molecules

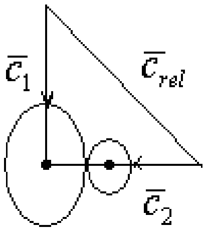
It is defined by the total number of collisions occurring per unit volume of the gas in unit time and it is symbolized by Z_{11}. Its expression is obtained when Z_1 is multiplied by $\frac{1}{2}N'$ and it is $Z_{11} = Z_1 \times \frac{1}{2}N'$.

The factor, $\frac{1}{2}$ ensures that the collision $A.....A'$ and $A'.....A$ are counted as only one collision. So, $Z_{11} = \sqrt{2}\,\pi\sigma^2\,\bar{c}\,N' \times \frac{1}{2}N'$. Thus the expression of frequency of binary collisions among the same molecules is $Z_{11} = \dfrac{1}{\sqrt{2}}\pi\sigma^2\,\bar{c}\left(N'\right)^2$.

Frequency of binary collisions among the different molecules

Let us first consider the number of collisions made by a single molecule of 1st type with 2nd type molecules in unit time, and it is $Z_{1(2)} = \pi\,\sigma_{12}^2\,\bar{c}_1\,N_2'$, where $\sigma_{12} = \dfrac{\sigma_1 + \sigma_2}{2}$, $\bar{c}_1$ is average speed of the 1st type molecules and N_2' is the number density of the 2nd type molecules. It is assumed that all molecules are at rest except one molecule of the 1st type is moving with average speed, $\bar{c}_1$.





When the false assumption of one molecule is moving and others are at rest is rectified, the $\bar{c}_1$ is replaced by $\bar{c}_{rel}$ and $\bar{c}_{rel} = \sqrt{\left(\bar{c}_1\right)^2 + \left(\bar{c}_2\right)^2} = \sqrt{\dfrac{8kT}{\pi m_1} + \dfrac{8kT}{\pi m_2}} = \sqrt{\dfrac{8kT}{\pi\,\mu}}$, where $\dfrac{1}{\mu} = \dfrac{1}{m_1} + \dfrac{1}{m_2}$ and $Z_{1(2)} = \pi\sigma_{12}{}^2\sqrt{\dfrac{8kT}{\pi\mu}}\,N_2'$, where μ is called reduced mass of the two molecules.

Thus the frequency of binary collisions among unlike molecules is given by $Z_{12} = \pi\,\sigma_{12}^2\,\bar{c}_{rel}\,N_2' \times N_1'$

or, $Z_{12} = \pi\ \sigma_{12}^2 \sqrt{\frac{8kT}{\pi\mu}}\ N_1' N_2'$ or, $Z_{12} = \pi \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \sqrt{\frac{8RT}{\pi}\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}\ N_1' N_2'$.

Frequency of collisions for two like molecules – A special case

When the two colliding molecules are same then $M_1 = M_2 = M$, $\sigma_1 = \sigma_2 = \sigma$ and $N_1' = N_2' = N'$. Then, $\sigma_{12}^2 = \sigma^2$, $\frac{1}{M_1} + \frac{1}{M_2} = \frac{2}{M}$ and $N_2' \times N_1' = (N')^2$.

Putting the conditions and multiplying by $1/2$ to avoid double counting of collisions for like molecules, we get

$$Z_{11} = \frac{1}{2}\pi\ \sigma^2\ \sqrt{2} \times \sqrt{\frac{8RT}{\pi M}}\ (N')^2 \quad \text{or,} \quad Z_{11} = \frac{1}{\sqrt{2}}\pi\ \sigma^2 \sqrt{\frac{8RT}{\pi M}}\ (N')^2 \quad \text{or,} \quad Z_{11} = \frac{1}{\sqrt{2}}\pi\ \sigma^2\ \bar{c}\ (N')^2$$

.

Mean-free path in a mixture of two gases

Mean-free path of 1st type of molecules is $\lambda_1 = \frac{\bar{c}_1}{Z_{1(1)} + Z_{1(2)}}$ and of 2nd type of molecules is $\lambda_2 = \frac{\bar{c}_2}{Z_{2(2)} + Z_{2(1)}}$,

where $Z_{1(2)}$ is the number of collisions made by a single molecule of the 1st type with the 2nd type of molecules and $Z_{2(1)}$ is the number of collisions made by a single molecule of the 2nd type with the 1st type of molecules in unit time respectively.

Effect of T and P on Z_1, Z_{11} and λ

For ideal gas, the equation is $PV = \left(\frac{N}{N_A}\right)RT$ or, $P = \left(\frac{N}{V}\right)\left(\frac{R}{N_A}\right)T$ or, $P = N'kT$ or, $N' = \frac{P}{kT}$.

So, $Z_1 = \sqrt{2}\,\pi\sigma^2\,\bar{c}\,N'$ or, $Z_1 = \sqrt{2}\,\pi\sigma^2\sqrt{\frac{8kT}{\pi m}}\left(\frac{P}{kT}\right)$ or, $Z_1 = \frac{\sqrt{2}\,\pi\sigma^2}{k}\sqrt{\frac{8k}{\pi m}}\left(\frac{P}{\sqrt{T}}\right)$ or, $Z_1 \propto \frac{P}{\sqrt{T}}$.

Z_1 is directly proportional to P at constant T and inversely proportional to the square root of T at constant P.

Again, $Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2\,\bar{c}\,(N')^2 = \frac{1}{\sqrt{2}}\pi\sigma^2\ \sqrt{\frac{8kT}{\pi m}}\left(\frac{P}{kT}\right)^2 = \left[\frac{1}{\sqrt{2}}\left(\frac{\pi\sigma^2}{k^2}\right)\sqrt{\frac{8k}{\pi m}}\right] \times \frac{P^2}{T^{3/2}}$ or, $Z_{11} \propto \frac{P^2}{T^{3/2}}$.

So, Z_{11} is directly proportional to the square of the pressure of the gas at constant temperature.

Thus, at constant T, if pressure of the gas is doubled, Z_{11} is increased by four times.

Mean-free path, $\lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2\,N'}$ or, $\lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2\left(P/kT\right)} = \frac{k}{\sqrt{2}\,\pi\sigma^2}\left(\frac{T}{P}\right)$ so, $\lambda \propto \frac{T}{P}$.

So, if pressure of the gas is doubled at constant temperature, mean-free path of the molecules becomes halved.
When P is constant, $\lambda \propto T$ and when T and P both vary, λ remains constant as $P \propto T$ at constant V.

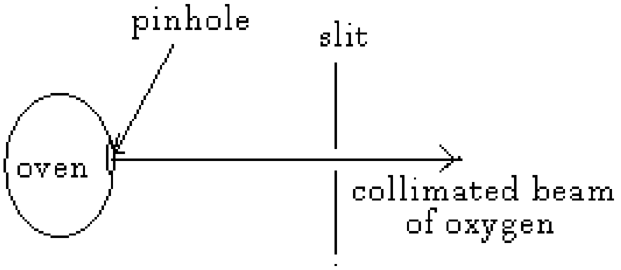
Problem:

(1) A stream of oxygen molecules at 500 K exit from a pin-hole in an oven and strikes a slit that selects the molecules to travel in a specific direction.
Given that the pressure outside of the oven is 2.5 × 10^{-7} atm, estimate the maximum distance at which the slit must be placed from the pin-hole in order to produce a collimated beam of oxygen molecules.
(Radius of O_2 = 1.8 × 10^{-10} m) **[IIT-JAM 2008, Q 41(a)]**

Solution:

The maximum distance between the pin hole and slit must be equal to the mean-free path so that within this distance the oxygen molecules suffer no collision and do not scatter from the path.

We have mean-free path, $\lambda = \dfrac{1}{\sqrt{2}\,\pi\sigma^2\,N'}$.



In the problem, $\sigma = 2\times1.8\times10^{-10}\,m$

$= 3.6\times10^{-8}\,cm$.

$$N' = \frac{P\,N_A}{RT}$$

$$= \frac{2.5\times10^{-7}\ atm\times6.023\times10^{23}\ mol^{-1}}{82\ atm\ cm^3\ mol^{-1}\ K^{-1}\times500\ K} = 3.67\times10^{12}\ cm^{-3}$$

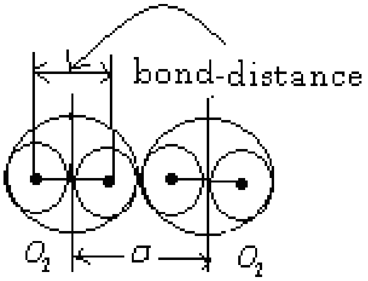
Hence, $\lambda = \dfrac{1}{\sqrt{2}\times3.14\times\left(3.6\times10^{-8}\,cm\right)^2\times3.67\times10^{12}\ cm^{-3}} = 47.3\,\text{cm}.$

Problem:(2) For O_2 gas at 25 °C and 1 atm, estimate the number of collisions made by a single molecule of O_2 in 1 sec and total frequency of collisions per cc per sec. The bond distance of O_2 = 1.2 Å.

Solution: The number of collisions made by a single O_2 molecule in one sec is $Z_1 = \sqrt{2}\,\pi\sigma^2\,\bar{c}\,N'$.

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8\times8.31\times10^7\ erg\ mol^{-1}K^{-1}\times298\ K}{3.14\times32\ gm\ mol^{-1}}} = 4.44\times10^4\,cm/\sec = 1598.4\ \text{Km / hr}.$$

$$N' = \frac{P\,N_A}{RT} = \frac{1.00\ atm\times6.023\times10^{23}\ mol^{-1}}{82\ atm\ cm^3\ mol^{-1}\ K^{-1}\times298\ K} = 2.465\times10^{19}\ cm^{-3}$$



The oxygen molecule is neither hard nor spherical, but reasonable estimate of σ in the hard sphere model might be twice the bond distance. Thus, σ = 2 ×1.2 Å = 2.4 Å = 2.4 × 10^{-8} cm. So,

$$Z_1 = \sqrt{2}\times3.14\times\left(2.4\times10^{-8}\,cm\right)^2\times4.44\times10^4\,cm\sec^{-1}\times2.465\times10^{19}\ cm^{-3} = 2.8\times10^9\ \sec^{-1} = 280\ crore/\sec.$$

Frequency of collisions, $Z_{11} = \dfrac{1}{2}N'Z_1 = \dfrac{1}{2}\times2.465\times10^{19}\ cm^{-3}\times2.8\times10^9\ \sec^{-1} = 3.4\times10^{28}\ cm^{-3}\sec^{-1}$.

Various properties of the gaseous state can be known from the above calculation for O_2 at 25 °C and 1.00 atm.

(i) Mean-free path (λ)

The value of mean-free path, $\lambda = \dfrac{\bar{c}}{Z_1} = \dfrac{4.44\times10^4\,cm/\sec}{2.8\times10^9\ \sec^{-1}} = 1.6\times10^{-5}\,cm$ = 1600 Å.

(ii) The average time between two successive collisions = $\dfrac{\lambda}{\bar{c}} = \dfrac{1}{Z_1} = \dfrac{1}{2.8\times10^9\ \sec^{-1}} = 4\times10^{-10}\sec$.

Special notes

(a) λ is small in comparison to the macroscopic dimension (say, 1 cm) of the container so that the molecules collide with each other far more often than with the walls of the container.

If the length of the two walls of the container is taken 1 cm, then the number of intermolecular collisions suffered within this distance = $\dfrac{1\,cm}{\lambda} = \dfrac{1\,cm}{1.6\times10^{-5}\,cm} = 6.25\times10^4 = 62500$.

The molecules suffer sixty two thousand five hundred collisions among themselves before colliding the walls.

(b) λ is large in comparison to the molecular diameter, as for O_2 it is 2.4 Å only.
So, a molecule moves a distance of many molecular diameters before colliding with another molecule.
Number of molecular diameters moves within $\lambda = \dfrac{1.6\times10^{-5}\,cm}{2.4\times10^{-8}\,cm} = 6.67\times10^{2} = 667$.

(c) λ is increased as P is lowered. A good vacuum is 10^{-6} torr $\approx 10^{-9}$ atm. Since $\lambda \propto \dfrac{1}{P}$ so, mean-free path of O_2 at 25 °C and 10^{-9} atm is $\dfrac{1.6\times10^{-5}\,cm}{10^{-9}\,atm}\times 1\,atm = 1.6\times10^{4}\,cm = 160\,m$. This is approximately 0.1 mile which is large compared with the usual container dimensions. So in a good vacuum, the gas molecules collide far more often with the container walls than one another. At 10^{-9} atm and 25 °C, one O_2 molecule makes only an average of $Z_1\times P = 2.8\times10^{9}\times10^{-9} = 2.8$ collision per sec with other gas molecules.

(d) Molar volume of O_2 gas at 25 °C and 1 atm is $\bar{V} = {RT}/{P} = \dfrac{82\,cc\ atm\ mol^{-1}K^{-1}\times 298\,K}{1\,atm} = 24,436\ cc\ mol^{-1}$.

Let the gas be in a cubic container. If the gas molecules are distributed uniformly in space with equal spacing between adjacent molecules, the gas volume can be divided into Avogadro number equal sized cubes.
The volume of each cube = $\dfrac{24,436\ cc\ mol^{-1}}{6.023\times10^{23}\,mol^{-1}} = 4.05\times10^{-20}\ cc$. If each cube contains a molecule at its centre, then the edge length of the cube is distance between the two molecules in the gas.
Thus, the distance between two molecules at 25 °C and 1 atm is $\left(4.05\times10^{-20}\,cc\right)^{1/3} = 3.44\times10^{-7}\,cm = 34.4$ Å.
λ is large in compared to the average distance between gas molecules.

(e) The frequency of wall collisions of oxygen molecules under the conditions of 25 °C and 1 atm pressure is
$Z_w = \dfrac{1}{4}\bar{c}\,N' = \dfrac{1}{4}\times 4.44\times10^{4}\,cm\ \sec^{-1}\times 2.465\times10^{19}\ molecules\ cm^{-3} = 2.74\times10^{23} collisions\ cm^{-2}\sec^{-1}$.

Ideal gas equation

A gas at equilibrium has definite value of pressure (P), volume (V), temperature (T) and composition (n). These are called state variables and are determined experimentally. The state of a gas can be defined by these variables and hence the name.

Earlier works of Boyle (1662), Charles (1787) and Avogadro (1811) give birth one equation of state for ideal gas.

Boyle's law: $V \propto \frac{1}{P}$, when n and T are fixed for the gas.

Charle's law: $V \propto T$, when n and P are fixed for the gas.

Avogadro's law: $V \propto n$, when P and T are kept constant for the gas.

When all variables are taken into account, the variation rule states that

$$V \propto \frac{1}{P} \times T \times n \quad \text{or,} \quad V = R \times \frac{1}{P} \times T \times n \quad \text{or,} \quad PV = nRT .$$

This is called ideal gas equation of state. This equation is found to hold good most satisfactorily when P → 0. At ordinary temperature and pressure, this equation is found to deviate about 0.5 %.
R is universal gas constant and its value is calculated from the statement that "at STP, one mole gas occupies 22.4 L".
Thus, the value of R is calculated as:

$$R = \frac{PV}{nT} = R = \frac{PV}{nT} = \frac{1atm \times 22.4L}{1mol \times 273K} = 0.082 \text{ L atm. mol}^{-1} \text{ K}^{-1}.$$

Other values are: $R = \frac{PV}{nT}$.

or, R = 8.31 J mol^{-1} K^{-1} = 1.98 cal mol^{-1} K^{-1} $\approx$ 2 cal mol^{-1}K^{-1}.

The above equation can be written as $PV = \left(\frac{w}{M}\right) \times RT$,

where w = weight of the gas in gm and M = molar mass of the gas.

Another form is, $P = \left(\frac{w}{V}\right) \times \frac{RT}{M}$.

But, $\frac{w}{V}$ = d, density of the gas at the temperature, T and pressure, P. Thus another form is,

$$P = \left(\frac{d}{M}\right) RT .$$

If the gas contains N number of molecules and N_A is the Avogadro number, then $N/N_A = n$,
so the other form is, $PV = \left(\frac{N}{N_A}\right) \times RT$ or, $P = \left(\frac{N}{V}\right)\left(\frac{R}{N_A}\right) \times T$ or, $P = N' kT$

where, N' = number of molecules per unit volume of the gas

and, k = Boltzmann constant = R/N_A = 1.38×10^{-16} erg molecule^{-1} K^{-1}.

Unit of P is dyne cm^{-2} in CGS system and Nm^{-2} = Pa in SI system.
1 torr = 1 mm of Hg so 1 atm = 760 torr. Again 1 bar = 10^5 Pa = 750 torr and 1Pa = 10 dyne cm^{-2} The moderate pressure is measured by manometer. Various gauges are used to measure low P.
P and T are intensive properties (independent of amount of the gas present in the container), while V is extensive property (dependent of the amount of the gas present in the container).

Problem: Calculate the number of molecules present per ml of an ideal gas maintained at a pressure of 7.6×10^{-3} mm of Hg at 0^{o}C. **[Burdwan Univ. 1985]**

Solution: Use the equation $PV = \left(N / N_A \right) RT$ and put $P = 7.6 \times 10^{-3} / 760 = 10^{-5}$ atm, $V = 10^{-3}$ L and R = 0.0821 L atm^{-1} mol^{-1} K^{-1}. . (Ans. 2.69×10^{14} molecules per ml.)

REAL GASES

Comparison between Ideal and Real gases

We may use one equation to distinguish an ideal gas from a real gas and this equation is

$$PV = nRT.$$

The gas which obeys this equation under all conditions of temperature and pressure is called **IDEAL GAS** and the gas which does not obey this equation at all temperatures and pressures is called **REAL GAS**.

A number of points can be discussed to compare these two types of gases.

Ideal gas

(1) The ideal gas can not be liquefied. As the gas has no intermolecular attraction so the molecules will not be condensed.

(2) Co-efficient of thermal expansion (α) depends solely on temperature (T) and does not depend on the nature of the gas. α is defined as, $\alpha = \frac{1}{V}\left(\partial V / \partial T \right)_P$.

For one mole ideal gas, PV = RT, hence $\left(\partial V / \partial T \right)_P = \frac{R}{P}$, so $\alpha = \frac{1}{V} \times \frac{R}{P} = \frac{R}{RT} = \frac{1}{T}$ i.e. $\alpha = \frac{1}{T}$.

This shows that all gases have the same co-efficient of thermal expansion at a given temperature.

(3) The co-efficient of compressibility (β) similarly is defined as, $\beta = -\frac{1}{V}\left(\partial V / \partial P \right)_T$.

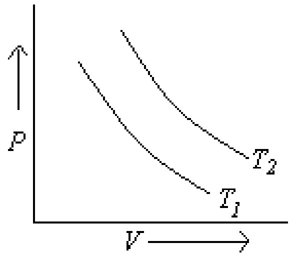
For ideal gas, PV = RT, so $\left(\partial V / \partial P \right)_T = -\frac{RT}{P^2}$ and $\beta = -\frac{1}{V}\left(-\frac{RT}{P^2} \right) = \frac{RT}{P^2 V} = \frac{PV}{P^2 V} = \frac{1}{P}$ or, $\beta = \frac{1}{P}$.

This shows also that β depends only on P of the gas and same for all gases.

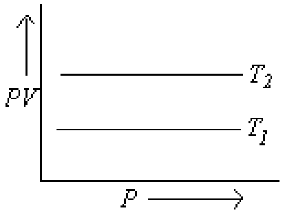
(4) When P is plotted against V at constant temperature, a rectangular hyperbola curve is obtained as given by Boyles law,

PV = constant at a given T.

The hyperbola curve at each temperature is called one isotherm and at different temperatures we have different isotherms. Two isotherms will never intersect.



(5) When PV is plotted against P at constant T, a straight line parallel to P-axis is obtained. At different temperatures, there will be different parallel lines.



(6) When an ideal gas passes through a porous plug, from higher pressure to lower pressure under insulated enclosure, there will be no change of temperature of the gas (J – T expansion). This confirms that ideal gas has no intermolecular attraction.

Real gas

(1) This gas could be liquefied since it has intermolecular attraction which helps to coalesce the gas molecules.

(2) The co-efficient of thermal expansion (α) is found to vary from gas to gas at a given temperature and hence it depends on the nature of the gas.

(3) The co-efficient of compressibility (β) also is found to depend on the nature of the gas at a given pressure.

(4) When P is plotted against V at a constant temperature, a rectangular hyperbola is obtained only at high temperature (above a certain temperature, called critical temperature, T_C of the gas). Tc is defined as the temperature above which the gas could not be liquefied what ever the pressure is applied. But at temperature below T_C, the gas is liquefied after certain pressure depending on temperature. It is discussed more elaborately under the head of **critical phenomena.**

(5) When PV is plotted against P for real gas, the following plots, called **Amagat's curves** are obtained.

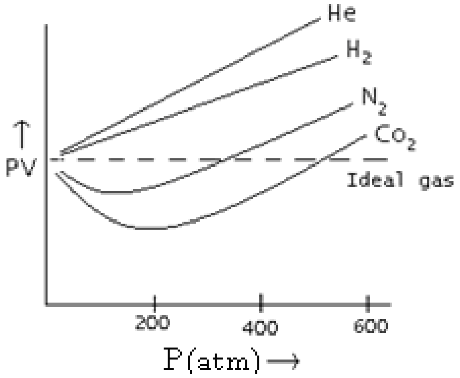


Fig.A : Amagat curves for different gases at a given temperature($0°C$)

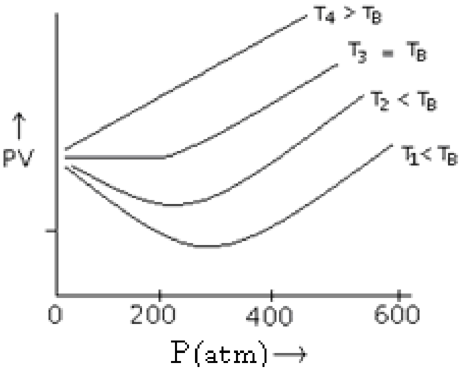


Fig.B : Amagat curves for a gas(CO_2) at different temperatures

Fig. A shows that for most gases, the value of PV decreases, attains minimum and then increases with increase of pressure. Only H_2 and He baffle this trend and the curve rises with increase of P from the very beginning.

Fig. B shows that for CO_2 gas, the depth of the minimum shifts towards the PV axis with increase of temperature. At T_3 temperature, PV curve runs parallel to P-axis up to certain range of P at low pressure region (P → 0). This temperature is called Boyle temperature (T_B) at which the real gas also obeys Boyle's law up to certain range of pressure at the low pressure region. The minimum coincides with the PV axis. The mathematical condition for calculation of Boyle temperature (T_B) is given by

$$\left[\frac{\partial(PV)}{\partial P}\right]_T = 0 \quad \text{when,} \quad P \rightarrow 0.$$

The curves obtained for H_2 and He at 0 ^oC is above their Boyle temperature and so with increase of P, value of PV increases from the start.

An important single parameter, called compressibility factor (Z) is used to measure the extent of deviation of the real gases from ideal behavior.

It is defined as, $Z = \frac{PV}{RT}$ where V is the molar volume of the gas at temperature T and pressure P.

When the value of Z = 1, the gas is ideal or there is no deviation of the gas from the ideal behavior.

When, $Z \neq 1$, the gas is non-ideal and departure of the value of Z from unity is a measure of the extent of non-ideality of the gas.

When $Z < 1$, the gas is more compressible than the ideal gas and

when $Z > 1$, the gas is less compressible than the ideal gas.

Since V is a function of T and P, Z is also a function of T and P, so Z may be defined as

$$Z = \frac{V}{V_{ideal}} \quad \text{and} \quad Z = \frac{P}{P_{ideal}}$$

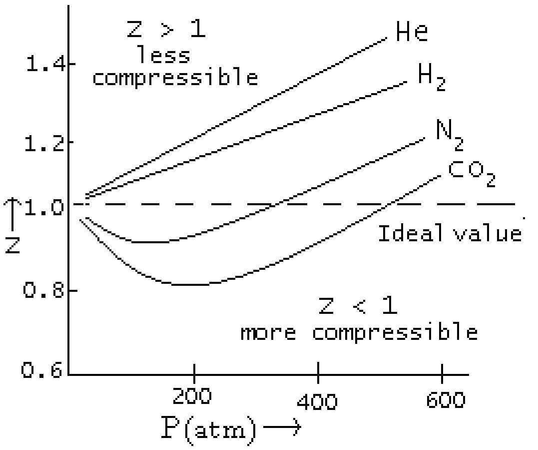
where, V_{ideal} is the molar volume of an ideal gas at the same T and P as the real gas.

Similarly P_{ideal} is the pressure of an ideal gas at the same T and V as the real gas.

When $Z < 1$, the gas exerts lower pressure than the ideal gas would and the volume of the gas becomes also lower than that of the ideal gas i.e. the gas becomes more compressible.

Similarly, when $Z > 1$ the gas exerts higher pressure than the ideal gas would and the volume of the gas becomes higher than that of the ideal gas i.e. the gas becomes less compressible.

Amagat curves can also be plotted as Z vs. P and similar curves are given below.



FigA: Amagat curves for different gasses at a given temperature (0 °C)

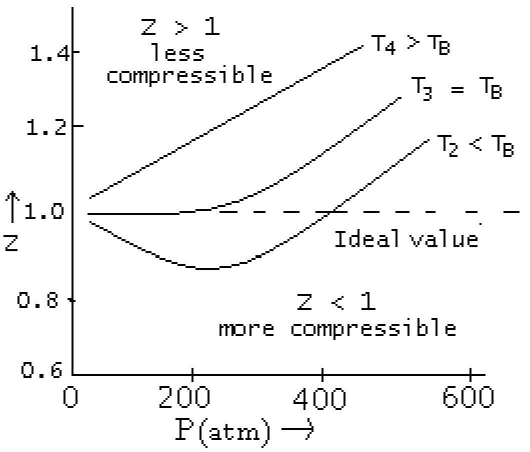


Fig B: Amagat curves for a gas (CO_2) at different temperatures

For N_2 gas at 50 ^oC, Z remains close to 1 up to nearly 100 atm.

(6) When real gases pass through porous plug from higher pressure to lower pressure under insulated condition, there occurs a drop of temperature. This is due to the fact that real gases have intermolecular attraction and when the gas expands, the molecules have to spend energy to overcome intermolecular attraction and so the temperature of the gas drops down.

Problem: Express the coefficient of thermal expansion (α) of a gas and show that α depends solely on T for an ideal gas. [**Ans.** See the Text.] **[Burdwan Univ. 1993]**

Question: Supposing that $P, \bar{V}$ are the pressure and molar volume of a real gas and $P_{id}, \bar{V}_{id}$ are those of an ideal gas at the same temperature, do you consider that $P_{id}\,\bar{V} = P\,\bar{V}_{id}$ = constant?

Draw a typical compressibility plot of Z vs. P for a real gas at ordinary temperature. Predict the values of Z for van der Waals equation of state at the limit P → ∞ and T → ∞. **[Burdwan Univ. 1997]**

Question: Two isothermals of a system do not intersect. Why? (1) **[Burdwan Univ. 2001]**

Answer: When two isothermals (P vs. V curves at two temperatures) intersect, two isothermals have the same temperature which is not possible.

Question: Draw curves to show the pressure dependence of compressibility factor (Z) of H_2 and He. **[Burdwan Univ. 2001]**

Question: What are the units of α and β where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$?

Give reasons for your answer. **[Burdwan Univ. 2001]**

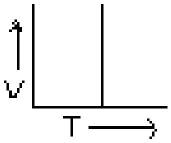
Question: Remark whether T_B should be higher than T_C. **[Burdwan Univ. 2002]**

Answer: T_B is greater than T_C of a gas as at T_C, both gas and liquid co-exist but at T_B only gas exists.

Question: Define compressibility factor. Draw the volume – temperature diagram for an isothermal expansion of a gas. (1).

Answer: For 1st part, see the Text.

When V is plotted against T, the curve is a straight line parallel to V-axis.



Reasons for deviation of real gases from ideal behavior

First in 1873, J.H. vander Waals, a Dutch scientist tried to explain the reasons for deviation of real gases from ideal gas equation. He modified the two assumptions in kinetic theory which are not exactly true. These incorrect assumptions are:

(a) The molecules are point-masses and thus molecules have definite masses but no volume.

(b) There is no intermolecular attraction in the gases.

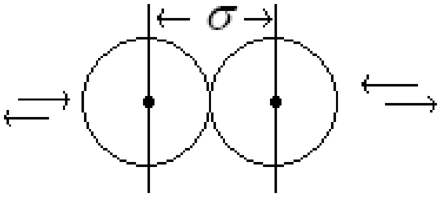
Vander Waals suggested that the gas molecules have definite size and he considered each molecule as rigid sphere. The volume of the gas molecules cannot be neglected especially when the gas is under considerable pressure. At N.T.P, the gas molecules occupy at least (1/1000) fraction of the total volume of the gas. But if pressure of the gas is raised to 10 atm, the gas molecules occupy (1/100) fraction of total volume of the gas (using molecular radius = $2\times10^{-8}cm$).

The gas could be liquefied and also be solidified. It is possible only if the molecules have strong cohesive forces. Joule-Thomson's porous-plug experiment definitely proves the existence of intermolecular attraction of the gases. Further if the gas molecules have no volume then when they condense to liquid or solid, how the liquid or solid acquire volume.

Definite size of the gas molecules results from the repulsive forces acting on the gas molecules when they are approaching close to make collisions. When two molecules approach to each other, they cannot reach closer together beyond a certain distance σ, called the distance of closest approach and it is also called collision diameter.

Higher the intermolecular repulsion, greater is the value of σ

The Vander Waals radius = $\sigma/2$.



Thus, it is obvious that gas molecules have both attraction and repulsion among themselves.

If there were no repulsion, the molecules would coalesce when they collide and the existence of gaseous phase would be at stake.

It is suggested that molecules initially attract each other as they approach and they repel each other when they collide. This happens due to the fact that attractive potential is long-range potential $\left(V_{attraction} \propto {}^{1}\!/_{r^6}\right)$ while the repulsive potential is short-range one $\left(V_{repulsion} \propto {}^{1}\!/_{r^{12}}\right)$, where r is the intermolecular distance between the molecules.

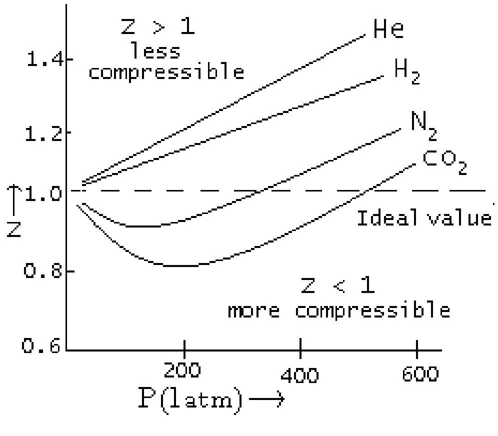
Qualitative explanation of Amagat's curves

The above concept of molecular attraction and repulsion can be used to explain the value of compressibility factor (Z) at least qualitatively.

(i) At low P (P → 0), the volume of the gas is large and so intermolecular distance (r) is large, both attractive and repulsive forces are negligibly small so it can not affect the ideal behavior. Z becomes one.

(ii) At moderate P, the molecules are not very close and long-range attractive potential dominates over the short-range repulsive potential.

The gas becomes more compressible and $Z < 1$.



(iii) At high P, the intermolecular distance (r) is small, the molecules are at very close to each other. At this condition, short-range repulsive potential dominates over the long-range attractive potential. The gas becomes less compressible than ideal gas (where there is no intermolecular interaction) and $Z > 1$.

For H_2 and He gases, attractive potential is very small in comparison to repulsive potential so $Z > 1$ always except when T is very low.

These intermolecular forces are popularly called van der Waals forces and these are responsible for the deviation of real gases from ideal behavior.

Formulation of van der Waals' equation

In 1873, van der Waals modified the ideal gas equation for 1 mole $P_{id}\bar{V}_{id} = RT$ by incorporating the size effect and intermolecular attraction effect of the real gases. These above two effects are discussed under the volume correction and pressure correction of the ideal gas equation.

Volume correction

In real gas, the molecules suffer strong repulsive forces when they come close and collide with each other. This repulsive force gives rise to definite size of the gas molecules. They have been assumed as rigid spheres.

The available volume for free movement of the molecules in real gas is less than $\bar{V}$. Let us take available space for free movement of 1 mole gas molecules ($\bar{V}_{id}$) = $\bar{V} - b$.

Where, $\bar{V}$ is molar volume of the gas and 'b' is volume correction term due to definite size of the gas molecules.

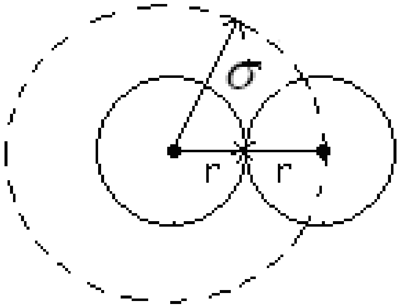
$\bar{V}_{id}$ is the molar volume of the ideal gas where gas molecules are regarded as point-masses.

It can be shown that 'b', called effective volume is four times the actual volume of one mole gas molecules.

Let us take σ is the collision diameter and r is the radius of each rigid sphere molecule and $\sigma = 2r$.

When two molecules encounter each other, the distance between the centre of the two molecules would be σ. They can not approach beyond this distance.

Thus, the sphere of radius σ (shown by dotted lines) will occupy a space unavailable for a pair of molecules.



Thus excluded volume = $\frac{4}{3}\pi\sigma^3$ for a pair of molecules.

Thus effective volume of a single molecule = $\frac{1}{2}\times\frac{4}{3}\pi\sigma^3 = \frac{2}{3}\pi\sigma^3$ and $b = \frac{2}{3}\pi N_A\sigma^3$ which is the effective volume of Avogadro number of molecules present in 1 mole gas. Thus,

$$b = \frac{2}{3}\pi N_A\sigma^3 \quad \text{or,} \quad b = 4\times\frac{4}{3}\pi N_A r^3 .$$

That is, 'b' is the four times the actual volume of one mole gas molecules.

The value of b is a measure of the size and it helps to calculate the radius of the gas molecules.

The van der Waals equation after volume correction becomes, $P_{id}\left(\bar{V} - b\right) = RT$.

Pressure correction

Pressure of a gas is developed due to the wall-collisions of the gas molecules. Magnitude of pressure of a gas depends on both the frequency of molecular collisions with the walls and the force of each collision. The magnitude of both the factors is reduced by intermolecular attraction. Thus, pressure exerted by the molecules in the real gas (P) will be less than that if there had not been intermolecular attraction as in the ideal gas (P_{id}).

Thus, $P_{id} > P$ or, $P_{id} = P + P_a$.

Where, P_a is the pressure correction term, called internal pressure originating from attractive forces between the molecules. Higher the intermolecular attraction in a gas, greater is the magnitude of P_a.

This reduction of pressure ($P_{id} - P = P_a$) acts with magnitude proportional to the density of the gas molecules. Both the frequency and force of each collision are reduced by intermolecular attraction, so the pressure is reduced in proportional to square of the gas density.

But density of gas is proportional to $1/\bar{V}$ so $P_a \propto 1/\bar{V}^2$ or, $P_a = a/\bar{V}^2$, where a is constant for the gas.

Greater the intermolecular attraction of the gas, higher will be the value of 'a'. Thus 'a' is a measure of intermolecular attraction of the gas.

Incorporating both the volume correction and pressure correction, the equation formed is called van der Waals equation for one mole gas.

$$\left(P + a/\bar{V}^2\right)\left(\bar{V} - b\right) = RT\ .$$

To convert the equation for n moles, $\bar{V}$ is to be replaced by V/n, where V is the volume of n moles of the gas.

Thus, van der Waals equation for n mole real gas is

$$\left(P + an^2/V^2\right)\left(V - nb\right) = nRT\ .$$

The reason for changing the volume is that it is an extensive property so it is changed when the amount is changed. The gas which obeys the van der Waals equation is called van der Waals gas.

Units of 'a' and 'b' in the equation:

From the van der Waals equation, we get $P_a = an^2/V^2$ or, $a = P_a \times V^2/n^2$

where, P_a is a pressure correction term and it has the unit of atm.

Thus, unit of $a = atm \times L^2/mol^2 = atm\, L^2\, mol^{-2}$.

Again, nb = unit of volume, so 'b' = L mol^{-1}.

In SI system, unit of 'a' = (N m^{-2}) m^6 mol^{-2} = N m^4 mol^{-2} and unit 'b' = m^3 mol^{-1}.

Significance of 'a' and 'b'

'a' term originates from the intermolecular attraction and $P_a = an^2/V^2$.

Thus 'a' is a measure of internal pressure of the gas and it measures the attractive forces between the molecules. Higher the value of 'a', greater is the intermolecular attraction and more easily the gas could be liquefied. Thus, $a_{CO_2} = 3.95\, atm\, L^2\, mol^{-2}$ and $a_{H_2} = 0.22\, atm\, L^2\, mol^{-2}$. CO_2 is more easily liquefied than H_2 gas.

Another constant, 'b' measures the molecular size and also a measure of repulsive forces.

The value of 'b' can be utilized to calculate the molecular diameter (σ). The greater the value of b, larger is the size of the gas molecule. Thus, $b_{CO_2} = 0.04\, L\, mol^{-1}$ and $b_{H_2} = 0.02\, L\, mol^{-1}$.

Let us consider two hypothetical cases to show the size effect and attraction effect on the pressure of the gas.

(a) For the real gas, $a = 0$ (i.e. no intermolecular attraction exist) but $b \neq 0$ (size is considered).

We have, van der Waals equation, $\left(P + an^2/V^2\right)\left(V - nb\right) = nRT$, but $a = 0$,

so, $P = \dfrac{nRT}{V - nb} > P_{id}$ since, $P_{id} = \dfrac{nRT}{V}$.

It means that the molecular size (repulsive interaction) creates higher pressure than that observed by the ideal gas where molecules have no volume.

(b) Again for a real gas, $a \neq 0$ (intermolecular attraction exists) but $b = 0$ (no size of the molecules)

The van der Waals equation, $P = \frac{nRT}{V} - \frac{an^2}{V^2} < P_{id}$, since $b = 0$ and $P_{id} = \frac{nRT}{V}$.

Thus intermolecular attraction effect reduces the pressure of the real gases.

Problem: Calculate the pressure of 2 moles of N_2 gas occupying 10 L volume at 27 °C using vander Waals equation. Given, $a = 1.4$ atm L^2 mol^{-2} and $b = 0.04$ L mol^{-1}.
Also calculate the pressure of the gas using ideal gas equation and find the extent of deviation from ideal behavior. [**Ans.** P = 4.904 atm, P_{id} = 4.92 atm and deviation = 0.325 %].

Calculation of Boyle Temperature (T_B)

Mathematical condition for calculation of Boyle temperature is, $\left[\frac{\partial(PV)}{\partial P}\right]_T = 0$, when P → 0.

The vander Waals equation is, $P = \frac{RT}{V-b} - \frac{a}{V^2}$ or, $PV = \frac{RTV}{V-b} - \frac{a}{V}$.

Thus $\left[\frac{\partial(PV)}{\partial P}\right]_T = \left[\frac{\partial(PV)}{\partial V}\right]_T \times \left(\frac{\partial V}{\partial P}\right)_T = \left[\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2}\right] \times \left(\frac{\partial V}{\partial P}\right)_T$

$$= \left[\frac{RT(V-b) - RTV}{(V-b)^2} + \frac{a}{V^2}\right] \times \left(\frac{\partial V}{\partial P}\right)_T = \left[-\frac{RTb}{(V-b)^2} + \frac{a}{V^2}\right] \times \left(\frac{\partial V}{\partial P}\right)_T.$$

When T = T_B, $\left[\frac{\partial(PV)}{\partial P}\right]_T = 0$ but $\left(\frac{\partial V}{\partial P}\right)_T \neq 0$, hence, $\frac{RT_B b}{(V-b)^2} = \frac{a}{V^2}$ or, $T_B = \frac{a}{Rb}\left(\frac{V-b}{V}\right)^2$.

Since P → 0, V is large and $\frac{V-b}{V} \approx 1$. Therefore, $T_B = {a}/{Rb}$

This is the expression of Boyle temperature for a gas obeying van der Waals equation.

Problem: Calculate ${a}/{b}$ for a gas for which T_B = 500K.

Solution: The Boyle temperature, $T_B = {a}/{Rb}$ so, ${a}/{b}$ = RT_B = 0.082 L atm mol^{-1} K^{-1} × 500K = 41 L atm mol^{-1}.

Problem: Explain the significance of Boyle temperature and hence deduce an expression for it from vander Waals equation. Comment on the possibility of defining a Boyle temperature if $a = 0$ and $a = b = 0$.

Solution: Last part of the question:
When $a = 0$, the van der Waals equation is, P (V – b) = RT or, PV = RT + Pb.
Differentiating with respect to P at constant T, we have $\left[\frac{\partial(PV)}{\partial P}\right]_T = b$.

But $b \neq 0$, hence $\left[\frac{\partial(PV)}{\partial P}\right]_T \neq 0$ at any temperature hence the gas have no Boyle temperature.

Again, when $a = b = 0$, the van der Waals equation is, PV = RT or, $\left[\frac{\partial(PV)}{\partial P}\right]_T = 0$.

This is zero at any temperature so any temperature is Boyle temperature for this gas.

Boyle temperature for several gases

Gases	He	H_2	N_2	Ar	CH_4	CO_2	C_2H_4	NH_3
T_B/K	23.8	116.4	332	410	506	600	624	995

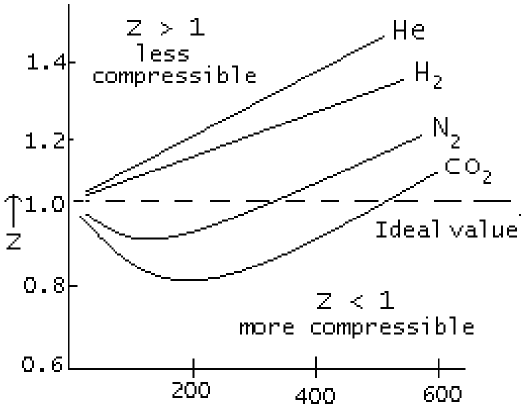
A quite accurate two-parameter equation of state for gases is the Reddlich-Kwong equation [O. Reddlich and J.N.S. Kwong, Chem. Review.44, 233 (1949)] is given as:

$$\left[P+\frac{a}{V(V+b)\sqrt{T}}\right](V-b)=RT \text{ for 1 mole gas.}$$

Which is useful over wide range of T and P. The Reddlich-Kwong parameters 'a' and 'b' differ in value for any gas from the van der Waals 'a' and 'b'.

Explanation of Amagat's Curves in the light of van der Waals equation

We have Amagat's curves, Z vs. P in two Figures:



FigA: Amagat curves for different gasses at a given temperature (0 °C)

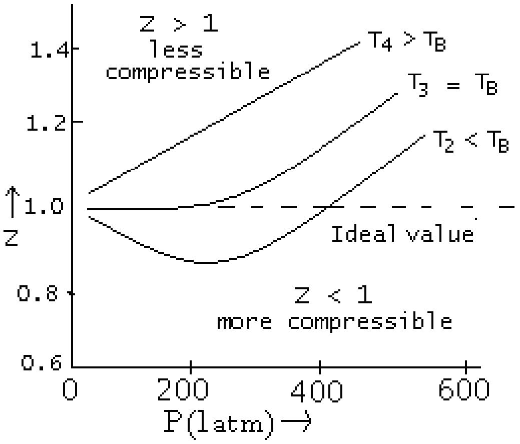


Fig B: Amagat curves for a gas (CO_2) at different temperatures

van der Waals equation for 1 mole real gas, $\left(P+a/V^2\right)(V-b)=RT$ or, $PV-Pb+a/V-ab/V^2=RT$.

Neglecting the small term ab/V^2, we get the equation as, $PV=RT+Pb-a/V$.

Replacing V in the correction term by ideal gas equation as $a/V=aP/RT$, and taking $Z=PV/RT$,

the expression of compressibility factor is $Z=1+\frac{1}{RT}\left(b-\frac{a}{RT}\right)P$. This shows that Z = f(T,P).

This equation can be used to explain Amagat's curves quantitatively at low P to moderate P region.

Fig. A: For CO_2 gas, 'a' is very high as we have seen that the gas is easily liquefiable.

Thus, $\frac{a}{RT}>b$ in the equation and. $b-\frac{a}{RT}=(-ve)$ Intermolecular attraction effect dominates over the size effect.

i.e. the slope of Z vs. P curve is (–ve) for CO_2 at moderate pressure region. This shows that the value of Z decreases with increase of P and it is found also in the curve.

For H_2 gas, 'a' is small as it is not easily liquefied $\frac{a}{RT}<b$ and the slope of Z vs. P curve for H_2 is (+ve). The value of Z increases with increase of P.

Fig. B: (i) When $T < T_B$, $T < \frac{a}{Rb}$ or, $b < \frac{a}{RT}$ and $b - \frac{a}{RT} = (-ve)$. It means that when $T < T_B$, the value of Z decreases with increase of P at the moderate pressures. The effect is due to the fact that intermolecular attraction dominates over the size effect.

So for CO_2, $Z < 1$ and the gas is more compressible.

(ii) When T = T_B = $\frac{a}{Rb}$ or, $b = \frac{a}{RT}$ or, $b - \frac{a}{RT} = 0$ and so Z = 1, the gas shows ideal behavior. The size effect compensates the effect due to intermolecular attraction of the gas. Z runs parallel to P-axis up to certain range of pressure at low pressure region.

(iii) When, $T > T_B$ means $T > \frac{a}{Rb}$ or, $b > \frac{a}{RT}$ and $b - \frac{a}{RT} = (+ve)$ i.e. Z increases with increase of P when $T > T_B$. The size effect dominates over the effect due to intermolecular attraction and $Z > 1$ and the gas is less compressible.

For H_2 and He, 0 ^oC is greater than their T_B values and so Z vs. P slope becomes (+ve).

At very low P ($P \rightarrow 0$) and at high T, volume is very large and both the size effect and attraction effect becomes negligible i.e. Pb and aP/RT are negligibly small and Z = 1. The gas behaves ideal.

Problem: The compressibility factor (Z) for one mole of a van der Waals gas at 0 ^oC and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant 'a'. **[IIT – JEE sample Question]**

Solution: We have $Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P$, but '$b$' is zero. So the compressibility factor, $Z = 1 - \frac{P}{RT} \times \frac{a}{RT}$.

$$\text{or, } a = (1-Z)\frac{(RT)^2}{P} = (1-0.5)\frac{\left(0.082\ L\ atm\ mol^{-1}K^{-1} \times 273K\right)^2}{100\ atm} = 2.50\ atm\ L^2 mol^{-1}.$$

Vander Waals constants 'a' and 'b' in real gas mixture:

For real gas mixture, V depends on mole fraction, as well as, on T and P.

The parameters 'a' and 'b' are taken as functions of the mixture's composition.

For a mixture of two gases, 1 and 2, it is useful to take

$$a = x_1^2 a_1 + 2x_1x_2\left(a_1a_2\right)^{1/2} + x_2^2 a_2 = \left(x_1\sqrt{a_1} + x_2\sqrt{a_2}\right)^2 \quad \text{and} \quad b = x_1b_1 + x_2b_2,$$

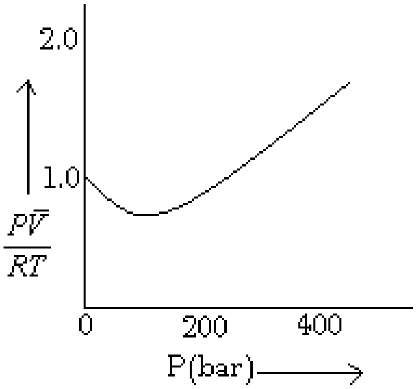
where x_1 and x_2 are the mole fractions of the components. 'b' is related to molecular size so is taken as weighted average of b_1 and b_2. The parameter 'a' is related to intermolecular attraction; the quantity $\left(a_1a_2\right)^{1/2}$ is an estimate of what the intermolecular attraction between gas 1 and gas 2 molecules might be.

In applying an equation of state to a mixture, V_m is replaced by V/n_{total} and $V = x_1\bar{V}_1 + x_2\bar{V}_2$.

This discussion explains that 'a' and 'b' do not follow the additivity rule.

Problem: The curve illustrates the $P\bar{V}$ behaviour of real gas, where $\bar{V}$ is the molar volume.

According to vander Waals for non-ideal gas behaviour, the values of one at high pressure are due to $\frac{P\bar{V}}{RT}$ greater than 1



(A) the effects of increased rate of collisions of the molecules with the walls of the container
(B) the effects of dissociation of individual gas molecules.
(C) the effects of the volume occupied by the gas molecules themselves.
(D) the effects of forces of attraction by the molecules.
(E) ideal gas behaviour in this pressure region. molecules with the walls of the container.

Question: A gas obeying the P(V – b) = RT has the compressibility factor, Z = 1.0018 at 27 ^{o}C and 1 atm pressure. Assuming the gas molecules to be spherical in shape, calculate its molecular diameter.

[Burdwan Univ, 2004]

Solution: $Z = 1 + b\left(\frac{P}{RT}\right)$. Putting the values, we get $b = 44.28$ cc/mol. But, $b = \frac{2}{3}\pi N_A \sigma^2$, again inserting the value of b, we get $\sigma = 3.275 \times 10^{-4}$ cm.

Critical phenomena – Andrews' curves

A gas can be liquefied by lowering temperature and increasing pressure. But influence of temperature is more important. Most gases are liquefied at ordinary pressure by suitably lowering of temperature. But a gas can not be liquefied unless its temperature is below a certain value depending on the nature of the gas. This temperature of the gas is called its critical temperature (T_C) and above which the gas can not be liquefied what ever high pressure may be applied to.

A gas can only be liquefied when the temperature is kept below T_C of the gas. The pressure required to liquefy the gas at its critical temperature is called critical pressure (P_C) and the volume occupied by one mole at T_C and P_C is called critical volume (V_C).

These critical constants can be illustrated from the Andrews curves. These curves are obtained by drawing P vs. V at different temperatures. T. Andrews (1869), in his experiment with one mole CO_2, collected data of P vs. V at various temperatures.

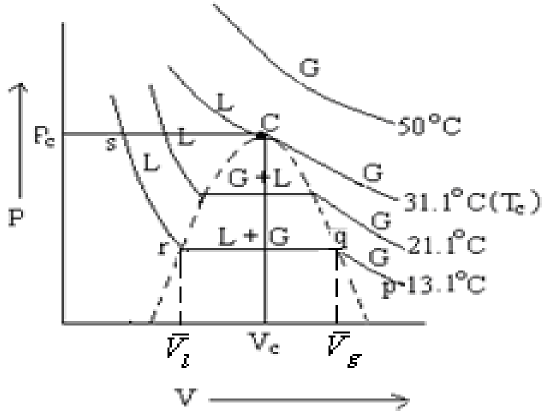
Let us discuss the isotherm (it is the curve describing the relation of P and V at constant T) at 13.1 ^{o}C (below T_C), pqrs. The point p represents the gaseous CO_2 at low pressure. As P is increased, V is correspondingly decreased according to Boyle's law.

At the point q, the gaseous CO_2 begins to liquefy and the pressure at the point is the saturation vapor pressure of CO_2.

As the volume is decreased, more of the gaseous CO_2 transforms into liquid CO_2 but P remains unchanged. This isothermal conversion continues up to r when all the gaseous CO_2 is converted into liquid CO_2. Now the curve rs is very steep as the liquid is highly incompressible.

When the temperature of 21.1 ^{o}C is taken for the study, similar curve is obtained except the liquid begins to form at higher saturation pressure and the range of volume over which condensation occurs is smaller.

At temperature 31.1 ^{o}C, the plateau shrinks to a point and this temperature is the critical temperature (T_C) of the gas.



T_c = 31.1°C, P_c = 72.9 atm and V_c = 94.2 cc/mol
(Andrew's isotherms for one mole CO_2)

The dotted line encloses a dome-shaped area within which liquid and gas are co-existent. The highest point C of the area indicates the critical point. On the right side of the area, gas alone is present and at the left liquid. Any point within the dome-shaped area represents the two phases, one liquid and one vapour in equilibrium to each other. The molar volumes of the liquid and vapour can be obtained by drawing a horizontal line to V-axis through the point representing the state of the system. The intersections with the boundary line correspond to molar volume of liquid ($\bar{V}_l$) and molar volume of vapour ($\bar{V}_g$),

respectively. This horizontal line is called tie line and it connects the state of one phase with the state of another phase and these phases are at equilibrium. As the temperature is increased, tie line becomes shorter and the molar volumes of the liquid and vapour approach each other, tending to be more alike and at the critical point C, the tie line vanishes, the distinction between liquid and vapour phase is lost.

When the temperature is further increased to 50 ^{o}C, the isotherm approaches more closely to that of ideal gas; no plateau is observed and no liquid is formed. Above T_C, there is a single gas phase.

Condition of the critical point (C)

The critical point is the limiting point of a series of horizontal two-phase lines. So the slope of the horizontal lines as well as the limiting point (C) is $\left(\partial P/\partial V\right)_T = 0$.

Again along the critical temperature isotherm, the slope is zero at the critical point (C) and is (–ve) on either side of the point. Thus the slope is maximum (zero value is greater than negative values) at the critical point. This slope is function of V and its derivative with respect to V is again zero at the point. That is, $\left[\frac{\partial}{\partial V}\left(\partial P/\partial V\right)_T\right]_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$ at the point.

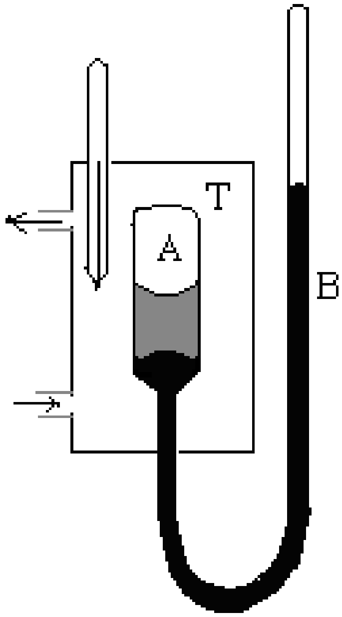
Thus, the condition of the critical point is given by,

$$\left(\partial P/\partial V\right)_T = 0 \qquad \text{and} \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0.$$

That means, both slope and curvature at the point is zero.

At the critical point, as $\left(\frac{\partial P}{\partial V}\right)_T = 0$ so, the isothermal compressibility $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ becomes infinite. As β is very large in the neighbourhood of the critical point, very little work is required to compress the vapour to liquid. This set up large differences in density in the neighbourhood of critical point. This difference makes spontaneous fluctuations in density which is accompanied by fluctuation of refractive index and light is scattered strongly. This is called critical opalescence.

Determination of critical temperature (T_C) and critical pressure (P_C)



These two properties of a real gas can be determined on the basis that at T_C and P_C, the density of liquid and vapour is identical and so the surface of separation of the two phases (meniscus) disappears.

(i) The bulb is enclosed by a jacket and its temperature can be varied according to requirements. A small quantity of the substance is enclosed over the mercury. This is attached to the manometer B in which a known amount of air is kept over mercury. Initially temperature is kept such that both liquid and vapour of the substance are present over the mercury. The surface of separation between the liquid phase and vapour phase should be clearly visible.

(ii) The temperature of the thermostat is gradually increased until the meniscus just disappears. The temperature and the corresponding pressure are noted from the thermometer and the manometer. Now the bulb is cooled slowly and again the temperature and pressure are noted down when the surface of separation just reappears. The mean of the two temperatures and pressures are the critical temperature (T_C) and critical pressure (P_C).

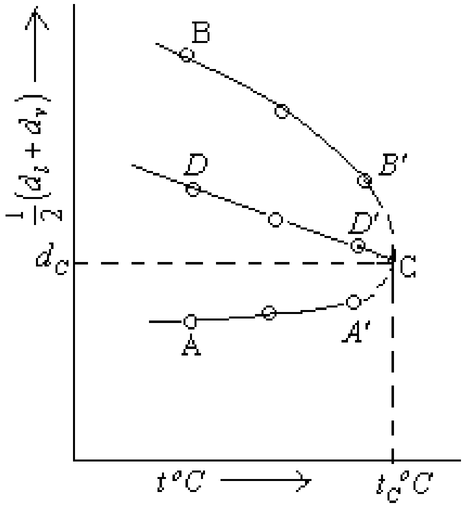
Determination of critical volume (V_C)

The determination of critical volume (V_C) is based on the basis of law of rectilinear diameters. According to the law, the mean value of the densities of the liquid and its saturated vapour of any substance is a linear function of temperature. These densities where liquid and vapour are at equilibrium are known as orthobaric densities.

Mathematically, we state the law as

$$\frac{1}{2}\left(d_l + d_v\right) = a + bt\,,$$

where a and b are constants. If a graph is drawn densities vs. temperature, the following curve is obtained. BB' curve for densities of liquid, AA' is for densities of saturated vapour and DD' for the mean density values. The point C, obtained by extrapolating the lines AA', BB' and DD', gives the critical density (d_C).



To determine the densities, a known mass of the liquid is taken in a graduated tube and sealed. It is heated to a particular temperature. The volumes V_l and V_v of liquid and vapour are read of from the graduation of the tube. If d_l and d_v are the densities of the liquid and vapour, respectively, then

$$m = V_l \times d_l + V_v \times d_v\,.$$

The experiment is repeated with different mass (m') of the liquid at the same temperature, then it becomes

$$m' = V_l' \times d_l + V_v' \times d_v\,.$$

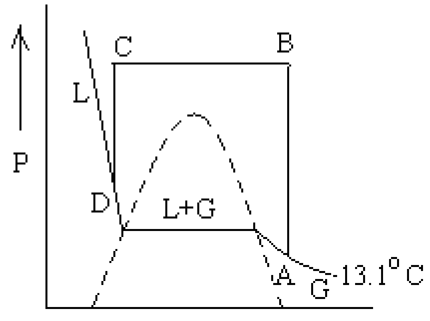
From these two equations, the value of d_l and d_v at the temperature is obtained. It is repeated at different temperatures to obtain the above curve.

The critical volume of the substance is then obtained by the relation, $V_C = \dfrac{M}{d_C}$.

Continuity of states:

In the Andrew's P –V diagram, the area in which the phases, gas and liquid coexist, are shown by dashed line. It is possible to make a sharp distinction between these two phases. Even the state point lies in the dashed area, the liquid and gas can be distinguished as there is surface of discontinuity and it separates the two phases. But it is not always possible to distinguish between gas and liquid. This is the principle of continuity of states.

In the adjoining figure, A and D lie on the same isotherm at temperature, 13.1 °C below the T_C of CO_2. The point A clearly indicates the gaseous state and point D indicates the liquid state. These two states are sharply defined and the dashed area which contains liquid-gas in equilibrium are also well-defined. But it is possible to shift from the gaseous state point A to the liquid state point D continuously without passing through the discontinuous dashed area.



Two phase-region and continuity of states

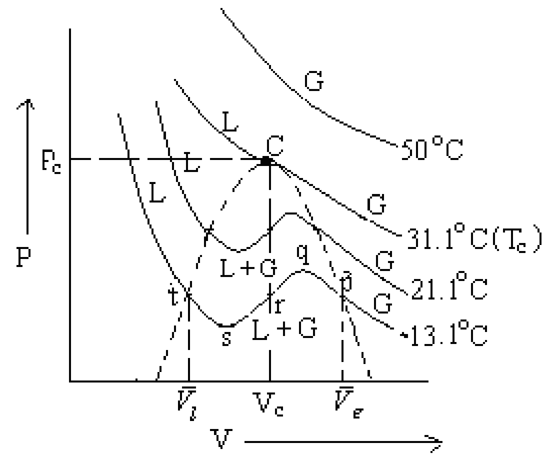
Let the gas at the state point A is heated to B at constant volume along AB. Then the gas is gradually cooled at constant pressure along BC, the volume reduced considerably. The gas is again cooled at constant volume until the state point D is reached. No where in the process liquid would appear. At D, the system is highly compressed gas. But the curve shows that this state point is for the liquid state. Thus there is hardly any difference between the liquid state and the gaseous state and there is no line of demarcation between the two phases. This is the continuity of states. The point D we may refer as liquid state or highly compressed gaseous state. In the absence of discontinuity there is no fundamental way of distinguishing liquid or gas. The gas is continuously transferred to the liquid without passing the usual process of condensation.

Critical phenomena and van der Waals equation

The van der Waals equation for one mole gas is, $P = \frac{RT}{V-b} - \frac{a}{V^2}$.

Taking the values of a and b for CO_2, it is possible to collect data P and V at temperatures 13.1 °C, 21.1 °C, 31.1 °C and 50 °C and to draw the similar isotherms like that of Andrew. These curves can be called van der Waals isotherms. The experimental Andrew's isotherms coincide with the van der Waals isotherms in all the points except the region where the gas and liquid are co-existing. The horizontal lines are replaced by wavy lines. These wavy portion of van der Waals curves poses two limitations of the van der Waals equation which are not realized in practice. The isotherm, pqrst shows that there are three volumes of the system at a given T and P. Again at the portion srq, it shows that with increase of pressure, volume is also increased. These two points show the limitations of van der Waals equation. How ever, pq and ts may be considered to represent the super saturation and unsaturation of the system.

With increase of temperature, the minimum and maximum points come close to each other and at the critical point, both coalesce. The slope and curvature both are zero at the point. Th



$T_c = 31.1°C$, $P_c = 72.9$ atm and $V_c = 94.2$ cc/mol
(van der Waals isotherms for one mole CO_2)

$$\left(\partial P \big/ \partial V\right)_T = 0 \qquad \text{and} \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 .$$

Relation between critical constants $\left(P_C,\ V_C\ and\ T_C\right)$ and van der Waals constants (a and b).

Differentiating van der Waals equation, $P = \frac{RT}{V-b} - \frac{a}{V^2}$ with respect to V at constant T, we get the slope,

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \quad \text{and the curvature,} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} .$$

But at the critical state, $\left(\partial P \big/ \partial V\right)_T = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$, and T = T_C, V = V_C.

Putting, we get, $\frac{RT_C}{\left(V_C - b\right)^2} = \frac{2a}{{V_C}^3}$ and $\frac{2RT_C}{\left(V_C - b\right)^3} = \frac{6a}{{V_C}^4}$. Solving the two equations, we get

$$V_C = 3b \qquad \text{and} \qquad T_C = \frac{8a}{27Rb} .$$

Again, the van der Waals equation at the critical point,

$P_C = \frac{RT_C}{V_C - b} - \frac{a}{{V_C}^2}$. Inserting the value of T_C and V_C , we have $P_C = \frac{a}{27b^2}$.

Thus, the relation between critical constants and van der Waals constants are:

$$V_C = 3b\,,\quad T_C = \frac{8a}{27Rb} \quad \text{and} \quad P_C = \frac{a}{27b^2}\ .$$

One property of the gas is critical coefficient, $\frac{RT_C}{P_C\,V_C}$. Putting V_C, P_C and T_C, $\frac{RT_C}{P_C\,V_C} = \frac{8}{3}$ = 2.66.

The value of compressibility factor at the critical state, $Z_C = \frac{P_C V_C}{RT_C} = \frac{3}{8}$ and it is less than 1.

This implies that at the critical state the gas is more compressible.

These values are tested experimentally whether the critical coefficient is constant and equal to 8/3 for all gases but it is found that it varies from gas to gas and the average value is about 3.66.

Unique application of these relations is the calculation of the van der Waals constants, a and b .

$b = \frac{V_C}{3}$, but V_C is avoided in the relation as it is not easily determined experimentally.

V_C is replaced by using the value of critical coefficient, $V_C = \frac{3}{8}\frac{RT_C}{P_C}$.

Therefore, the van der Waals constants are: $b = \frac{1}{8}\frac{RT_C}{P_C}$ and $a = \frac{27}{64}\frac{R^2T_C^2}{P_C}$.

The critical constants of a gas can be determined experimentally and so the value of the van der Waals constants, a and b can be calculated.

Problem: The van der Waals equation of a gas is given by, $\left(P + \frac{0.00786}{V^2}\right)(V - 0.00224) = 0.0041(273 + t)$ where P is in atm and V in lit. Find the values of P_C and T_C. **[NET]**

Solution: Comparing with van der Waals equation, $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$,

nR = 0.0041 or, n × 0.082 = 0.0041 or, n = 0.05. Now,

nb = 0.00224 or, 0.05 b = 0.00224 or, b = 0.0448 lit mol^{-1}.

Again, an^2 = 0.00786 or, a × $(0.05)^2$ = 0.00786, or, a = 3.14 atm lit^2 mol^{-2}.

So, $P_C = \frac{a}{27b^2} = \frac{3.144}{27\times(0.0448)^2} = 58.028\,atm$ and $T_C = \frac{8a}{27Rb} = \frac{8\times 3.144}{27\times 0.082\times 0.0448} = 253.58K$.

Problem: Calculate the radius of Argon atom, given its critical temperature and pressure as – 122 °C and 48 atm respectively. Assume that Argon obeys van der Waals equation of state. [**Burdwan Univ. 1994]**

Solution: The van der constant, $b = \frac{1}{8}.\frac{RT_C}{P_C}$. Putting the data given in the problem, we get

$$b = \frac{1}{8}.\frac{0.082\,L\,atm\,mol^{-1}K^{-1}\times(273-122)K}{48\,atm} = 0.0322\,L\,mol^{-1} = 32.2 \text{ cc mol}^{-1}.$$

But, $b = 4\times N_A\frac{4}{3}\pi r^3$ or, 32.2 cm^3 mol^{-1} = 4 × 6.023×10^{23} × (4/3) × 3.14 × r^3 or, r = 1.5 × 10^{-8} cm.

Hence the radius of the Argon atm = 1.5 × 10^{-8} cm.

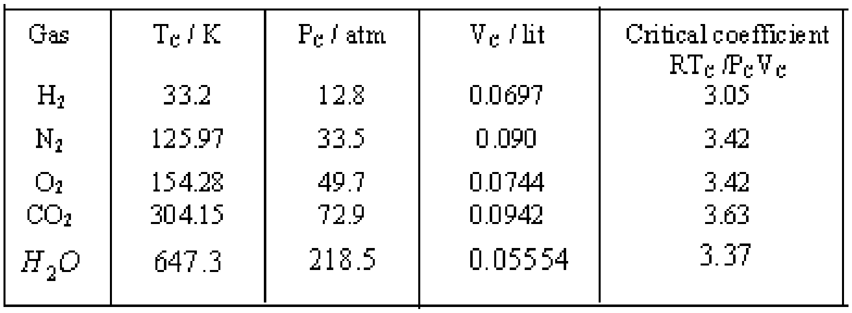
Question: A scientist with a simple view of life proposes the following equation for one mole gas.

$$P = \frac{RT}{V} - \frac{B}{V^2} + \frac{C}{V^3}.$$

Express P_C, V_C T_C in terms of B and C and find the expression of critical compressibility factor, (Z_C).

[$Ans. V_C = \frac{3C}{B}, T_C = \frac{B^2}{3RC}$ and $P_C = \frac{B^3}{27C^2}$ **,** $z_C = \frac{1}{3}$ **.]**

Table showing the values of critical constants of different gases including their critical coefficients



Gas	T_c / K	P_c / atm	V_c / lit	Critical coefficient $RT_c / P_c V_c$
H_2	33.2	12.8	0.0697	3.05
N_2	125.97	33.5	0.090	3.42
O_2	154.28	49.7	0.0744	3.42
CO_2	304.15	72.9	0.0942	3.63
H_2O	647.3	218.5	0.05554	3.37

Reduced form of vander Waals equation of state

Vander Waals equation can be expressed in terms of their reduced variables in stead of T, P and V. The reduced variables are defined as the actual variables divided by the corresponding critical constants.

Thus, reduced pressure, $\pi = P/P_C$, reduced temperature, $\theta = T/T_C$ and reduced volume, $\varphi = V/V_C$.

Replacing P, V and T in the van der Waals equation by corresponding reduced variables, we have

$$\left[\pi P_C + \frac{a}{(\varphi V_C)^2}\right](\varphi V_C - b) = R\theta T_C \cdot$$

Inseting the value of critical constants, $V_C = 3b$, $T_C = \frac{8a}{27Rb}$ and $P_C = \frac{a}{27b^2}$ in the above equation,

we get the reduced form of van der Waals equation,

$$\left(\pi + \frac{3}{\varphi^2}\right)(3\varphi - 1) = 8\theta \cdot$$

The important feature of the equation is that it is independent of van der Waals constants, a and b.

Thus it appears that the equation is independent of the nature of the gas and general as it is in ideal gas equation. But it is not true. The characteristic gas constants now remain in disguise within the reduced variables (π, φ and θ) as these variables contain critical constants (P_C, V_C and T_C) and these are characteristic constants of the gas. Thus it is not that generality lost in van der Waals equation is regained in this form. However, the reduced equation is more general than any specific equation of state.

Law of corresponding states:

The reduced equation of state, $\left(\pi + \frac{3}{\varphi^2}\right)(3\varphi - 1) = 8\theta$

gives birth one important generalization, called law of corresponding states. If the two substances have the same reduced pressure (π) and are also in the same reduced temperature (θ), then their reduced volumes (φ) should be the same and the substances are said to be in their corresponding states. Thus, two gases are at the same reduced temperature and under same reduced pressure so they are in corresponding states and have same reduced volume. This principle of corresponding states is not exact, but it is the single most important basis for evaluation and comparison of different physical properties of substances. All substances will appear to behave similarly at their corresponding states.

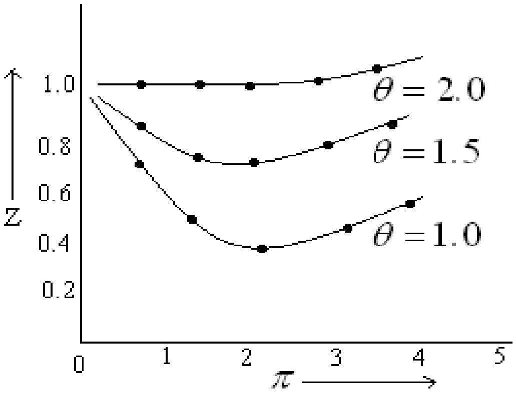
For example, argon at 302K (T_C = 151K) and under 16 atm (P_C = 48 atm) pressure and ethane at 381 K (T_C = 190.5K) and 18 atm (P_C = 54 atm) are in their corresponding states, since each has

$$\theta = 2 \quad \text{and} \quad \pi = 1/3.$$

This principle is approximately valid for gasses composed of spherical and non-polar molecules.
The important utility of the law is that any physical property can be compared among the substances when they are in corresponding states. Let us illustrate it with the value of compressibility factor (Z) of different gasses at their corresponding states.

We have by definition, $Z = \dfrac{PV}{RT} = \dfrac{\pi P_C \times \varphi V_C}{R \times \theta T_C}$ or, $Z = \dfrac{P_C V_C}{R T_C} \times \dfrac{\pi \varphi}{\theta}$ or, $Z = \dfrac{3}{8} \times \dfrac{\pi \varphi}{\theta}$.

Since $\dfrac{\pi \varphi}{\theta}$ is same for the gasses in the corresponding state so the gases have same value of Z. This implies that all gases deviate from ideal behavior to the same extent when they are in corresponding state. Thus when Amagat's curves are drawn Z vs. π at constant θ, all gases produce single curve as due to the same value of Z. The curves are drawn taking the average value of Z at the corresponding state of different gases as the law is approximately obeyed. This shows that, all substances behave almost similarly like the value of Z at the corresponding states.



Limitations of vander Waals equation

(1) The equation predicts $V_C = 3b$ but the mean value is $V_C = 2b$.

(2) The equation also suggests that $\dfrac{RT_C}{P_C V_C}$ = 8/3 = 2.66 but the average value is 2.66.

(3) T_B/T_C = 27/8 = 3.375, but the value is about 2.98.

So we can conclude that van der Waals equation explains the behavior of the real gas qualitatively but it fails to explain quantitatively.

Question: For an ideal gas, critical temperature is 0 K. – Comment on the statement. **[Burdwan Univ.1992]**

Answer: The statement is correct. This can be shown as follows.

The ideal gas equation for one mole is PV = RT or P = RT / V. Now taking 1st and 2nd derivatives of P with respect to V at constant temperature and setting to zero at the critical point, we have,

$$-\frac{RT_C}{V_C^{\,2}} = 0 \ \ and \ \ \frac{2RT_C}{V_C^{\,3}} = 0 \ . \quad \text{Subtracting,} \quad T_C\left(\frac{2R}{V_C^{\,3}} + \frac{R}{V_C^{\,2}}\right) = 0 \quad \text{or, } T_C = 0\text{K.}$$

Kammerlingh – Onnes Virial equation:

The equation of state of a gas can be satisfactorily expressed as a power series of volume or pressure as suggested by H. Kammerlingh – Onnes in 1901 as,

$$PV = RT\left[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + ...\right]$$

where, B is 2nd virial coefficient and is most important in the expression. B, C, D is the virial coefficients and dependent of T and on the nature of the gas, their values are small in magnitude.
Virial equation as power series of P is given by

$$PV = RT\left[1 + B_1P + C_1P + D_1P + ...\right].$$

Vander Waals equation of real gas can be recast in virial form as follows:

The equation, $P = \dfrac{RT}{V-b} - \dfrac{a}{V^2}$ or, $PV = \dfrac{RTV}{V-b} - \dfrac{a}{V} = \dfrac{RT}{\left(1-b/V\right)} - \dfrac{a}{V} = RT\left(1-b/V\right)^{-1} - \dfrac{a}{V}$.

or, $PV = RT\left(1+\dfrac{b}{V}+\dfrac{b^2}{V^2}+\dfrac{b^3}{V^3}+......\right)-\dfrac{a}{V} \approx RT\left(1+\dfrac{b}{V}\right)-\dfrac{a}{V} \approx RT + RT\left(b-\dfrac{a}{RT}\right)\dfrac{1}{V}$.

So the virial form of van der Waals equation as power series of V is $Z \approx 1+\left(b-\dfrac{a}{RT}\right)\dfrac{1}{V}$.

The 2nd virial coefficient, $B = b - \dfrac{a}{RT}$. Thus, evaluation of B is possible from a and b.

At the Boyle temperature, (T_B), B = 0, and thus, $b - \dfrac{a}{RT_B} = 0$ or, $T_B = \dfrac{a}{Rb}$.

Therefore the virial form of the vander Waals equation can produce the expression of T_B.
The above virial form can easily be expressed as power series of P by replacing by

$V = \dfrac{RT}{P}$ (Taking approximation for small term). So the form is, $Z = 1+\dfrac{1}{RT}\left(b-\dfrac{a}{RT}\right)P$.

A more rigorous mathematical treatment can be exercised to get a form consisting of 3rd virial coefficient. This form is,

$$Z = 1+\frac{1}{RT}\left(b-\frac{a}{RT}\right)P+\frac{a}{\left(RT\right)^3}\left(2b-\frac{a}{RT}\right)P^2.$$

It can be shown that the 2nd virial coefficient is (–ve) while 3rd virial coefficient is (+ve).
Thus, when P is low, 2nd term dominate and Z decreases with increase of P but when P is high, the 3rd term dominates and Z increases with the increase of P in the Z vs. P diagram.
A complete description of Z vs. P curve is obtained by this virial form of van der Waals equation.
More accurate virial form of van der Waals equation is

$$Z = 1+\frac{1}{RT}\left(b-\frac{a}{RT}\right)P+\frac{a}{\left(RT\right)^3}\left(2b-\frac{a}{RT}\right)P^2+\frac{a}{\left(RT\right)^4}\left[3b^2-\frac{2a^2}{\left(RT\right)^2}\right]P^3$$

Problem: What is the molar volume of N_2(g) at 500 K and 600 bar according to (a) ideal gas law and (b) the virial equation? The virial coefficient, B of N_2(g) at 500 K is 0.0169 L $mol^{-1.}$

Solution: (a) The molar volume, $V = \dfrac{RT}{P} = \dfrac{0.08314 L\,bar\,K^{-1}mol^{-1}\times 500K}{600\,bar} = 6.92\times10^{-2}\,L\,mol^{-1}$

(b) $Z = 1+\dfrac{BP}{RT} = 1+\dfrac{\left(0.0169 L\,mol^{-1}\right)\times\left(600\,bar\right)}{0.08314 L\,bar\,K^{-1}mol^{-1}\times 500K} = 1.244$.

Now, $V = \dfrac{ZRT}{P} = \left(1.244\times6.92\times10^{-2}\right) = 8.62\times10^{-2}\,L\,mol^{-1}$.

Formulation of virial form, $Z = 1+\dfrac{1}{RT}\left(b-\dfrac{a}{RT}\right)P+\dfrac{a}{\left(RT\right)^3}\left(2b-\dfrac{a}{RT}\right)P^2$

K' Onnes virial form as power series of P is, $Z = 1+B_1P+C_1P^2+D_1P^3 ----$(A)

But the van der Waals equation for one mole is, $PV = RT\left(1-b/V\right)^{-1}-\dfrac{a}{V}$ (See the last page).

or, $$Z=\left(1-b/V\right)^{-1}-\frac{a}{RTV}=\left[1+\frac{b}{V}+\left(\frac{b}{V}\right)^{2}+\left(\frac{b}{V}\right)^{3}+----\right]-\frac{a}{RTV}$$

$$=1+\left(b-\frac{a}{RT}\right)\frac{1}{V}+\left(\frac{b}{V}\right)^{2}+\left(\frac{b}{V}\right)^{3}+--.$$

Replacing $V=\frac{ZRT}{P}$, $$Z=1+\frac{1}{RT}\left(b-\frac{a}{RT}\right)\frac{P}{Z}+\left(\frac{b}{RT}\right)^{2}\frac{P^{2}}{Z^{2}}+\left(\frac{b}{RT}\right)^{3}\frac{P^{3}}{Z^{3}}+-- \qquad \text{(B)}$$

Equating with equation (A), we have,

$$B_1P+C_1P^2+D_1P^3----=\frac{1}{RT}\left(b-\frac{a}{RT}\right)\frac{P}{Z}+\left(\frac{b}{RT}\right)^{2}\frac{P^{2}}{Z^{2}}+\left(\frac{b}{RT}\right)^{3}\frac{P^{3}}{Z^{3}}+--$$

Dividing both by P, $$B_1+C_1P+D_1P^2----=\frac{1}{RT}\left(b-\frac{a}{RT}\right)\frac{1}{Z}+\left(\frac{b}{RT}\right)^{2}\frac{P}{Z^{2}}+\left(\frac{b}{RT}\right)^{3}\frac{P^{2}}{Z^{3}}+--. \qquad \text{(C)}$$

But, when P → 0, Z → 1. Using this condition, we get 2nd virial coefficient, $B_1=\frac{1}{RT}\left(b-\frac{a}{RT}\right)$.

Putting this expression in (D), $$B_1+C_1P+D_1P^2----=B_1\frac{1}{Z}+\left(\frac{b}{RT}\right)^{2}\frac{P}{Z^{2}}+\left(\frac{b}{RT}\right)^{3}\frac{P^{2}}{Z^{3}}+--,$$

or, $$B_1\left(1-\frac{1}{Z}\right)+C_1P+D_1P^2----=\left(\frac{b}{RT}\right)^{2}\frac{P}{Z^{2}}+\left(\frac{b}{RT}\right)^{3}\frac{P^{2}}{Z^{3}}+--.$$

Again dividing by P, we have $$B_1\left(\frac{Z-1}{P}\right)\frac{1}{Z}+C_1+D_1P----=\left(\frac{b}{RT}\right)^{2}\frac{1}{Z^{2}}+\left(\frac{b}{RT}\right)^{3}\frac{P}{Z^{3}}+-- \qquad \text{(D)}$$

From (A), $\frac{Z-1}{P}=B_1+C_1P+D_1P^2+---$, but, when P → 0, Z → 1, so, $\frac{Z-1}{P}=B_1$.

Using this value of B_1 in (D), we get $$\frac{B_1^{\,2}}{Z}+C_1+D_1P--=\left(\frac{b}{RT}\right)^{2}\frac{1}{Z^{2}}+\left(\frac{b}{RT}\right)^{3}\frac{P}{Z^{3}}+--.$$

Again, using the condition, P → 0, Z → 1, we get $B_1^{\,2}+C_1=\left(\frac{b}{RT}\right)^{2}$ or, $C_1=\left(\frac{b}{RT}\right)^{2}-B_1^{\,2}$.

Inserting $B_1=\frac{1}{RT}\left(b-\frac{a}{RT}\right)$, we get $C_1=\frac{a}{(RT)^3}\left(2b-\frac{a}{RT}\right)$.

Putting the values of B_1 and C_1 in (A) and keeping up to 3rd term, the required expression of Z is,

$$Z=1+\frac{1}{RT}\left(b-\frac{a}{RT}\right)P+\frac{a}{(RT)^3}\left(2b-\frac{a}{RT}\right)P^2\cdot$$

Question: The compressibility factor (Z) for one mole of a van der Waals gas at 0 ^{o}C And 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the vander Waals constant ‘ a ’. **[IIT – JEE Sample Question]**

Answer: We have, $Z=1+\frac{1}{RT}\left(b-\frac{a}{RT}\right)P=1-\frac{P}{RT}\times\frac{a}{RT}$, (as b in the van der Waals gas is assumed to be 0)

or, $a=(1-Z)\frac{(RT)^2}{P}$. Putting, Z = 0.5, R = 0.082 L atm mol^{-1}K^{-1}, T = 273K and P = 100 atm,

we get, a = 2.5 atm L^2 mol^{-2}.

Question: An approximate expression for the compressibility factor (Z) of van der Waals gas is

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)P^2$$

with terms having usual significance.
At what temperature does the slope of the Z vs. P curve (at P → 0) have maximum value?
What is the value of maximum slope? **[Burdwan Univ. 1995, 2001]**

Answer: 1st Part : The slope of the Z vs. P curve is $\left(\partial Z/\partial P\right)_T$ and let it be S. Thus, from the expression of Z, we get, $S = \frac{1}{RT}\left(b - \frac{a}{RT}\right) + \frac{2a}{(RT)^3}\left(2b - \frac{a}{RT}\right)P$. But the slope at P → 0, $S_0 = \frac{1}{RT}\left(b - \frac{a}{RT}\right)$.

It is seen that S_0 is a function of T only. Now putting the condition of extrema, we have

$$\frac{dS_0}{dT} = -\frac{b}{RT^2} + \frac{2a}{R^2T^3} = 0 \quad \text{or,} \quad \frac{b}{RT^2} = \frac{2a}{R^2T^3} \quad \text{or,} \quad T = \frac{2a}{Rb}.$$

It could be shown that at this temperature, S_0 attains maximum by using 2nd derivative of S_0 with respect to T and then equating to zero.

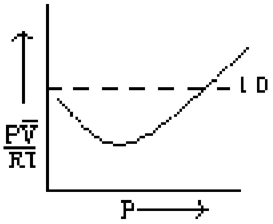
2nd Part: The value of the maximum slope, is obtained by inserting $T = \frac{2a}{Rb}$ in the expression of the slope,

$$S_0 = \frac{1}{RT}\left(b - \frac{a}{RT}\right) \text{ and it is } S_0 = b^2/4a.$$

Question: Draw a graph $P\bar{V}/RT$ vs. P for a real gas. Remark on its nature for a general case. If a gas obeys the equation, $P\bar{V}/RT = 1 + \alpha P + \beta P^2$, show that the following restrictions are imposed on α and β.

(i) $\alpha < 0$ and $\beta > 0$ (ii) $4\beta > \alpha^2$. **[Burdwan Univ. 2004]**

Answer: 1



2nd part: The value of $P\bar{V}/RT$ = 1 when P → 0 and then decreases, attains minimum and then increases with increase of P.

3rd part: (i) For the restriction on α and β, let

$$Z = 1 + \alpha P + \beta P^2 \quad \text{where, } Z = P\bar{V}/RT.$$

For the minimum value of Z, the conditions are $dZ/dP = \alpha + 2\beta P = 0$ and $d^2Z/dP^2 = 2\beta = (+ve)$.

Thus, β = (+ve). Now, $\alpha + 2\beta P = 0$ or, $\alpha = -2\beta P = (-ve)$ as β = (+ve) so, $\alpha = (-ve)$.

Thus, restrictions $\alpha < 0$ and $\beta > 0$ are fulfilled.

(ii) Again since $\alpha + 2\beta P = 0$ or, $P = -\alpha/2\beta$. Putting this expression, we get the minimum value of Z as

$$Z_{\text{min.}} = 1 + \alpha\left(-\alpha/2\beta\right) + \beta\left(-\alpha/2\beta\right)^2 = 1 - \frac{\alpha^2}{2\beta} + \frac{\alpha^2}{4\beta} = 1 - \frac{\alpha^2}{4\beta}.$$

But, $Z_{\text{min.}} = (+ve) > 0$, so, $1 - \frac{\alpha^2}{4\beta} > 0$ or, $1 > \frac{\alpha^2}{4\beta}$ or, $4\beta > \alpha^2$.

Question: A gas obeying the P (V − b) = RT has the compressibility factor, Z = 1.0018 at 27 °C and 1 atm pressure. Assuming the gas molecules to be spherical in shape, calculate its molecular diameter. **[Calcutta Univ. 2004]**

Answer: $Z = 1 + b\left(P/RT\right)$. Putting the values, we get b = 44.28 cc/mol. But $b = \left(2/3\right)\pi N_A \sigma^3$, again inserting the value of b , we get, $\sigma = 3.275 \times 10^{-8}\ cm$.

Problem: The critical density of CO_2 is 0.45 gm/cc; calculate the constant 'b' for the gas in dm^3 $mole^{-1}$.

[Burdwan Univ. 1996]

Solution: The critical volume of CO_2, $V_C = \dfrac{M}{d_C} = \dfrac{44\ gm\ mol^{-1}}{0.45\ gm\ cc^{-1}} = 97.78$ cc. Again, $V_C = 3b$ cc mol^{-1}.

Thus, $b = V_C/3 = 32.59$ cc mol^{-1} = 0.03259 dm^3 mol^{-1}. [1 dm^3 = 1 litre 10^3 cc.]

Problem: Using the above value of b, calculate the collision diameter (σ) of CO_2 molecules.

Solution: The relation is $b = \dfrac{2}{3}\pi N_A \sigma^3$ or, $\sigma = \left(\dfrac{3b}{2\pi N_A}\right)^{1/3} = \left(\dfrac{3\times 32.59\ cm^3\ mol^{-1}}{2\times 3.14\times 6.023\times 10^{23}\ mol^{-1}}\right)^{1/3} = 2.96\times 10^{-8}\ cm$.

Question: Express the compressibility factor Z of a van der Waals gas in terms of reduced temperature (θ) and reduced pressure (π).

Answer: For van der Waals gas, $Z = \dfrac{PV}{RT} = \dfrac{V}{V-b} - \dfrac{a}{RTV} = \left(1-\dfrac{b}{V}\right)^{-1} - \dfrac{a}{RTV}$. Replacing V by $\dfrac{RT}{P}$,

or, $Z = \left(1-\dfrac{bP}{RT}\right)^{-1} - \dfrac{aP}{(RT)^2}$. Now, putting $b = \dfrac{RT_C}{8P_C}$ and $a = \dfrac{27R^2T_C{}^2}{64P_C}$, we get $Z = \left(1-\dfrac{\pi}{8\theta}\right)^{-1} - \dfrac{27\pi}{64\theta^2}$.

Dieterici equation

The ideal gas equation is $P_{id}V_{id} = RT$, where V_{id} is the volume of 1 mole gas in which the molecules are assumed as point masses and thus it is the free space for the movement of molecules. P_{id} is the pressure of the gas in which the intermolecular attraction is assumed to be zero and so the molecules can exert full thrust on the walls of the gas container during their wall-collisions.

When the equation is used for real gas, correction of the above two assumptions are needed.

Volume correction

In Dieterici equation for real gas, the volume correction is same as that done in van der Waals equation and it is $V_{id} = V - b$, where V is the volume of 1 mole real gas and b is the effective volume of Avogadro number of molecules .

Pressure correction

In real gas, the molecules suffer attraction among themselves. The molecules which are inside the interior (bulk) of the gas, each molecule are surrounded by other molecules uniformly and the resultant attractive force on the molecule becomes nil. It means that the molecules in the interior behave like ideal gas. But at the exterior (near the wall), the molecule must have excess potential energy (A) to escape attraction of neighbouring molecules and hit wall.

Thus the number density near the walls (N') is less than that in the bulk (N'_{id}).

So, $$\frac{N'}{N'_{id}} = \frac{P}{P_{id}} = e^{-A/RT} \quad \text{or,} \quad P_{id} = P\times e^{A/RT},$$

where P_{id} is the pressure that the molecules would exert if there had not been any molecular attraction (ideal pressure) and P is the pressure when the molecules suffer attraction (real pressure).

A is the excess potential energy of the molecules per mole of the real gas.

Incorporating these two corrections, we have Dieterici equation as

$$P\times e^{A/RT}(V-b) = RT \quad \text{or,}\ P(V-b) = RT\,e^{-A/RT}.$$

It is expected that A is inversely proportional to molar volume, V and so $A \propto \dfrac{1}{V}$ or $A = \dfrac{a}{V}$, where a is characteristic constant of the gas but its value is not same as that in van der Waals equation.

The Dieterici equation then becomes $P(V-b) = RT\,e^{-a/RTV}$.

The values of a and b are determined experimentally by fitting to data.

Dieterici equation and van der Waals equation

We have the Dieterici equation, $P = \frac{RT}{V-b}e^{-a/RTV}$. Expanding the equation, we get

$$P = \frac{RT}{V-b}\left(1-\frac{a}{RTV}+\frac{1}{2}\left(\frac{a}{RTV}\right)^2-.....\right) = \frac{RT}{V-b}\left(1-\frac{a}{RTV}\right).$$ [Neglecting higher terms]

So, the Dieterici equation is P = $\frac{RT}{V-b}-\frac{a}{V\left(V-b\right)}$. But at low pressures, the volume is large and so $V\left(V-b\right) \approx V^2$. Putting this approximation, we get $P = \frac{RT}{V-b}-\frac{a}{V^2}$ or, $\left(P+\frac{a}{V^2}\right)\left(V-b\right) = RT$ which is van der Waals equation.

So, the Dieterici equation and van der Waals equation would respond to the same extent at low pressures.

The validity of the Dieterici equation can be compared by average experimental value and calculated value of the properties like Boyle temperature, critical co-efficient, V_C/b of the gases, etc. These values we first calculate using Dieterici equation and then match with average experimental values of the various gases.

Relation between critical constants $\left(V_C, T_C, P_C\right)$ and Dieterici constants (a and b)

Putting $\frac{a}{RT} = c$ in the Dieterici equation, we get $P = \frac{RT}{V-b}e^{-\frac{c}{V}}$.

Now, $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{\left(V-b\right)^2}e^{-\frac{c}{V}} + \frac{RT}{V-b}e^{-\frac{c}{V}}\left(\frac{c}{V^2}\right) = -\frac{P}{\left(V-b\right)}+P\times\frac{c}{V^2}$ and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = -\frac{1}{V-b}.\left(\frac{\partial P}{\partial V}\right)_T + \frac{P}{\left(V-b\right)^2} + \frac{c}{V^2}\left(\frac{\partial P}{\partial V}\right)_T - \frac{2Pc}{V^3} = \left(\frac{\partial P}{\partial V}\right)_T\left[\frac{c}{V^2}-\frac{1}{V-b}\right] + P\left[\frac{1}{\left(V-b\right)^2}-\frac{2c}{V^3}\right].$$

At the critical point, both 1st and 2nd derivative would be zero, and P = P_C, V = V_C, and T = T_C,

thus, $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P_C}{\left(V_C-b\right)}+P_C\times\frac{c}{{V_C}^2} = 0$ and so $\frac{P_C}{\left(V_C-b\right)} = P_C\times\frac{c}{{V_C}^2}$ or, $\frac{1}{\left(V_C-b\right)} = \frac{c}{{V_C}^2}$ ……..(a)

Again, $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T\left[\frac{c}{{V_C}^2}-\frac{1}{V_C-b}\right]+P\left[\frac{1}{\left(V_C-b\right)^2}-\frac{2c}{{V_C}^3}\right] = 0$ or, $\frac{1}{\left(V_C-b\right)^2} = \frac{2c}{{V_C}^3}$ ……….(b).

From (a) and (b), we get $V_C = 2b$, and at the critical temperature,

$c = \frac{a}{RT_C}$, so from (a), $c = \frac{{V_C}^2}{\left(V_C-b\right)} = \frac{{V_C}^2}{\left(V_C-b\right)} = \frac{4b^2}{2b-b} = 4b$, thus $\frac{a}{RT_C} = 4b$ or, $T_C = \frac{a}{4Rb}$.

At the critical pressure, $P_C = \frac{RT_C}{V_C-b}.e^{-a/RT_CV_C} = \frac{a}{4b}.\frac{1}{2b-b}.e^{-4b/2b}$ or, $P_C = \frac{a}{4b^2}.e^{-2}$.

Thus, the relations are $V_C = 2b$, $T_C = \frac{a}{4Rb}$ and $P_C = \frac{a}{4b^2}.e^{-2}$.

Critical co-efficient = $\frac{RT_C}{P_C V_C} = \frac{a}{4b}\times\frac{1}{2b}\times\frac{4b^2}{a}e^2 = \frac{1}{2}e^2 = 3.695$.

Boyle temperature (T_B)

When Dieterici equation is multiplied by V, we get $PV = \frac{RTV}{V-b}\times e^{-a/RTV}$.

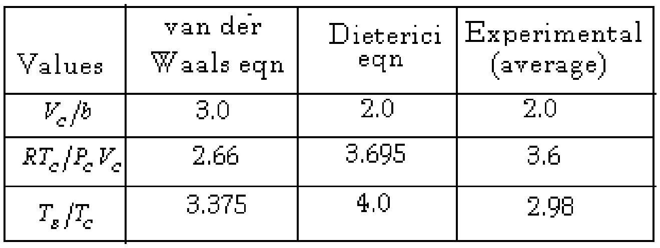
So, $\left[\frac{\partial(PV)}{\partial P}\right]_T = \left[\left(\frac{RT}{V-b}-\frac{RTV}{(V-b)^2}\right)e^{-a/RTV} + \frac{RTV}{(V-b)}\times\frac{a}{RTV^2}\times e^{-a/RTV}\right]\left(\frac{\partial P}{\partial V}\right)_T$. But $\left(\frac{\partial P}{\partial V}\right)_T \neq 0$

At the Boyle temperature, $\left[\frac{\partial(PV)}{\partial P}\right]_T = 0$ and $T = T_B$ so, $\frac{RT_B}{V-b}-\frac{RT_BV}{(V-b)^2}+\frac{RT_BV}{(V-b)}\times\frac{a}{RT_BV^2} = 0$,

or, $\frac{RT_BV}{V-b}\left[\frac{1}{V}-\frac{1}{V-b}-\frac{a}{RT_BV^2}\right] = 0$ or, $\frac{a}{RT_BV^2} = \frac{1}{V-b}-\frac{1}{V} = \frac{b}{V(V-b)}$ or, $RT_B = \frac{a(V-b)}{bV}$.

But for the condition of Boyle temperature, $P \to 0$ and V is very large so, $V - b \approx V$, and. $T_B = \frac{a}{Rb}$.

Comparison of the equations with experimental values



Values	van der Waals eqn	Dieterici eqn	Experimental (average)
V_c/b	3.0	2.0	2.0
RT_c/P_cV_c	2.66	3.695	3.6
T_B/T_c	3.375	4.0	2.98

The table shows that Dieterici equation is better but it has also limitations. However, van der Waals equation is simple and easy to handle mathematically.

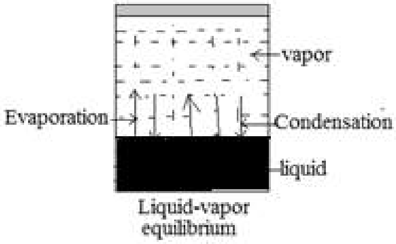
THE LIQUID STATE OF MATTER

Introduction: This state of matter has definite volume but no definite shape. It takes the shape of the container in which it is kept. This is due to the more intermolecular attraction than the gaseous state but less than the solid state. In gas, the molecules are in a state of random motion as there is small intermolecular attraction while in liquid state, randomness of the molecules are in less random state. Liquid can flow like the gas and so these two are called fluid. From the above consideration, it is concluded that most properties of the liquid arise due to nature and magnitude of the intermolecular forces between the molecules. The important properties which we shall discuss in the chapter are:
(A) Vapor pressure (B) Viscosity (C) Surface tension one after another.

(A) VAPOR PRESSURE OF LIQUIDS:

When a liquid is added into a closed evacuated container at constant temperature, we find that some molecules of the liquid pass from the surface into the space above it spontaneously. This is called evaporation. The molecules in the vapor phase collide with each other and also with the wall of the container like the gas. Some of the molecules in the vapor phase collide on the surface of the liquid and come back to the liquid phase. This is called condensation. Evaporation and condensation go on simultaneously. A stage is ultimately reached when the rate of evaporation is equal to the rate of condensation and a dynamic equilibrium is set-up between the liquid and its vapor.

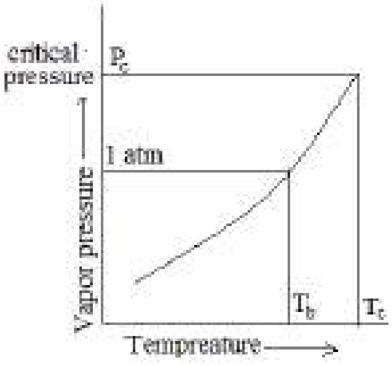
$$\text{Liquid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{Vapor}$$



At the equilibrium, the number density of molecules of the liquid phase and of the vapor phase remains unchanged.
The molecules in the vapor phase are in chaotic random motion. They are colliding with the walls of the container and exert some pressure. At equilibrium, this pressure is called vapor pressure of the liquid and this pressure is the characteristic property of the liquid at a given temperature. Thus vapor pressure of a liquid can be defined as the pressure exerted by the vapors that are in equilibrium with the liquid at a given temperature. The vapor pressure of the liquid depends on:

(i) the nature of the intermolecular forces in the liquid, higher the intermolecular forces in the liquid less will be evaporation and low is the vapor pressure of the liquid and

(ii) temperature. With increase in temperature, average kinetic energy of the molecules is increased. The increased KE partly overcomes the intermolecular attractive forces in the liquid enhancing the escaping tendency of the molecules. There occurs more evaporation and this results an increase of equilibrium vapor pressure of the liquid.



The vapor pressure of the liquid can be determined by manometer. Other several methods are there such as barometric method, isoteniscopic method, Ramsay and Young method etc.
The vapor pressure of a liquid is determined at different temperature and when these vapor pressures are plotted against temperature, we have the above type exponential curve.
The vapor pressure of the liquid is increased exponentially with temperature. The temperature at which the vapor pressure of the liquid becomes equal to the superincumbent pressure (usually atmospheric pressure), the liquid starts boiling. So the boiling point of a liquid is the temperature at which its vapor

pressure is equal to the external pressure. When the external pressure is one atmospheric pressure, it is called the normal boiling point of the liquid. It is the characteristic constant of the liquid.
The quantitative relation of variation of vapor pressure (p) of a liquid with temperature (T) is given by Clapeyron equation (derived in the chapter, Chemical Thermodynamics)

$$\frac{dp}{dT} = \frac{\bar{L}_{vap}}{T\left(\bar{V}_g - \bar{V}_l\right)}$$

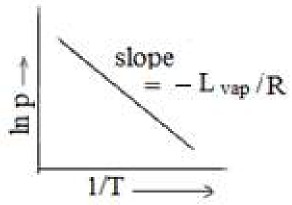
where $\bar{L}_{vap}$ is the molar latent heat of vaporization, $\bar{V}_g$ and $\bar{V}_l$ are the molar volume of vapor and liquid respectively. Since $\bar{V}_g >> \bar{V}_l$ so we can neglect $\bar{V}_l$ in comparison to $\bar{V}_g$, and we get

$\frac{dp}{dT} = \frac{\bar{L}_{vap}}{T\bar{V}_g}$. If we assume the vapor obeys ideal gas equation, then, $\bar{V}_g = \frac{RT}{p}$ and the equation becomes

$$\frac{dp}{dT} = \frac{\bar{L}_{vap}\,p}{RT^2} \text{ or, } \frac{dp}{p} = \frac{\bar{L}_{vap}}{R}\frac{dT}{T^2} \text{ or, } \int \frac{dp}{p} = \frac{\bar{L}_{vap}}{R}\int \frac{dT}{T^2} \text{ or, } \ln p = -\frac{\bar{L}_{vap}}{R}\left(\frac{1}{T}\right) + \ln A \text{ or, } p = Ae^{-\bar{L}_{vap}/RT}$$

(assuming $\bar{L}_{vap}$ to remain independent of T) and $\ln A$ is constant.

The equation shows that $\ln p$ is a function of reciprocal of T.
When $\ln p$ is plotted against 1/T, it gives a straight line from the slope of which we can get the value of $\bar{L}_{vap}$.
Again, if p is plotted against T, the curve will be exponential type same as that obtained from the experimental data.



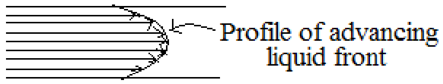
The equation can be integrated within limits, $\int_{p_1}^{p_2} \frac{dp}{p} = \frac{\bar{L}_{vap}}{R}\int_{T_1}^{T_2} \frac{dT}{T^2}$ or, $\ln\frac{p_2}{p_1} = \frac{\bar{L}_{vap}}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$.

$\bar{L}_{vap}$ is assumed to remain constant between the temperature T_1 and T_2. p_1 and p_2 are the vapor pressure of the liquid at temperatures T_1 and T_2 respectively.
This equation is helpful to determine molar latent heat of vaporization of a liquid by measuring vapor pressures at two temperatures.

(B) VISCOSITY OF LIQUIDS:

Resistance to flow exhibited by liquids is known as viscosity. Because of this property some liquids flow slowly than the others. For example, glycerene, castor oil, etc flow slowly while ether, ethanol, water, etc flow rapidly. Former liquids are called high viscous liquids while the latter liquids are called low viscous liquids.

Flow of a liquid in a pipe: When a liquid flows through a pipe, all parts of the liquid do not move with equal velocity. A thin layer immediate in contact with the wall of the pipe remains almost stationary. The velocity of flow of successive layers from the wall of the pipe increases and reaches maximum for the center layer.



Laminar flow of liquid in a tube

Thus there is velocity gradient, $\left(dv_x/dz\right)$ of the flowing liquid.

v_x is the velocity of layer along x- axis (along the pipe) and z is the distance of the layer from the wall of the pipe

Origin of viscosity in liquid:

When a higher moving layer slides over the lower moving layer, there occurs internal friction between the layers. Due to this internal friction, slower moving layer exerts resistance to the faster moving layer and the flow of the higher moving layer is retarded. This internal friction originates in liquid due to intermolecular attraction between the layers. This is evidenced by the fact that viscosity of the liquid decreases with increase of temperature, i.e.$\frac{\partial \eta}{\partial T}$ = (-ve).

Co-efficient of viscosity: Newton's law of viscous flow is given by $f_v = -\eta A\left(\frac{dv_x}{dz}\right)$,

where η is the viscosity coefficient of a liquid. It is the characteristic constant of the liquid at a given temperature and pressure. It is a measure of the viscosity of a liquid. Higher the value of η of a liquid, slower is its flowing tendency.

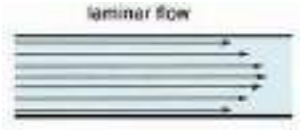
The unit of η in CGS system is poise according to the name of the scientist, Poiseuille which is equal to dyne cm^{-2} sec and in SI system it is Pa. s which N m^{-2} sec. 1 Pa.s = 10 poise.
The dimension of η is M L^{-1} T^{-1} or M/LT.

Fluidity (φ) of a liquid is the reciprocal of viscosity (η) i.e., $\varphi = \frac{1}{\eta}$. It measures the flowing tendency of a liquid.

Kinematic viscosity: In some fluid-flow, the ratio of viscous force (η) to the inertia force (ρ) is important. Flow depends, apart from (η), on density (ρ). The ratio (η / ρ) is thus defined as kinematic viscosity of the liquid. This viscosity is very often used in engineering work to compare the flowing property of different liquids. It is defined as, kinematic viscosity = viscosity coefficient (η) / density.
It is expressed in stoke unit. One stoke = (gm $cm^{-1}sec^{-1}$)/gm cm^{-3} = cm^2 sec^{-1}.
Mass factor of the liquid is absent in this viscosity of the liquid.

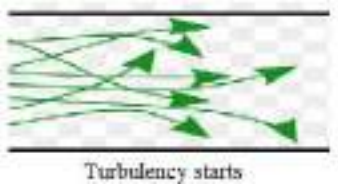
Type of liquid-flow:

(i) Laminar flow: When the viscosity of discharge of a liquid in a tube is low, all the layers of the liquid move parallel to each other. This flow is called laminar flow or streamlined flow (lamina $\rightarrow$ $layer$).



The velocity of the fluid (both liquid and gas) at any particular point is always same in magnitude and direction. Hence two streamlines do not cross each other.
Newton's law of viscous flow is only applicable to this laminar flow.

(ii) Turbulent flow:



When the rate of discharge of the moving liquid is high, the condition of streamline flow is not maintained and turbulent (broken) flow starts. The streamlines crowd as the velocity of flow increases. The velocity of the liquid at a point varies with time irregularly.

Reynold Number (R_e):

Reynold suggested that when the value, $\frac{d\rho u}{\eta}$, a dimensionless quantity, called Reynold number (R_e) exceeds a certain value (≈ 1150), turbulent flow starts.

Thus, $R_e = \dfrac{d\rho u}{\eta}$, where a liquid of viscosity coefficient, η and density, ρ flows through a tube of diameter, d with velocity u . R_e is dimensional quantity since $\dfrac{d\rho u}{\eta} = \dfrac{cm \times gmcm^{-3} \times cmsec^{-1}}{gmcm^{-1}sec^{-1}}$ = unitless so dimensional quantity.

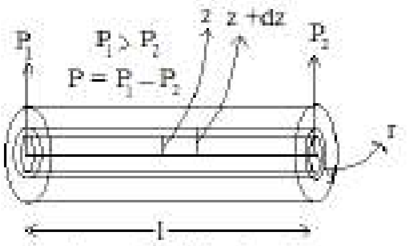
Approximately, the following conditions are followed for the liquid-flow. When,

$R_e < 1000$, laminar flow occurs.
$R_e \approx 1000 – 1500$, turbulent flow starts, a transition zone.
$R_e > 1500$, definite turbulent flow persists.

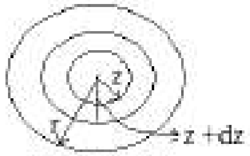
Thus when a capillary tube is used, d is very small and the flow becomes streamlined especially when the velocity of discharge of the liquid through the capillary is low. This is why capillary tube is used in the measurement of viscosity of a liquid.

Formulation of Poiseuille Equation, $\left[\eta = \dfrac{\pi \mathrm{P} r^4 t}{8lV}\right]$:

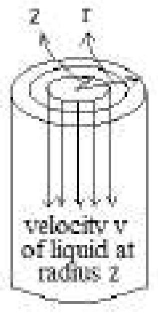
Let us consider the streamline flow of an incompressible fluid (here we take liquid) through a capillary tube of radius r which is large compared to the mean free path of the liquid (so that molecules cannot bounce between the walls which they invariably do in diffusive flow). Let the length of the tube be l . Fluid at the wall is at rest and the velocity of liquid is maximum at the centre of the tube. Let v be the velocity of the layer at any distance z from the central axis and it varies from 0 to r .



velocity profile in laminar flow



cross-section of the tube



velocity v of liquid at radius z

Newton's law viscous flow for laminar flow, $f_d = \eta A\left(\dfrac{dv_x}{dz}\right)$, where $\left(\dfrac{dv_x}{dz}\right)$ = velocity gradient and as z increases v_x increases, f_d = driving force of the liquid flow and A = area of the contact of layers.

Let us consider the liquid layer which is z distance away from the centre of the tube. For this layer, the above equation becomes as : $f_d = P \times \pi z^2$, where $P = P_1 - P_2$ = pressure difference of the two ends of the tube.

$A = 2\pi zl$ and $\left(\dfrac{dv_x}{dz}\right) = \left(-\dfrac{dv}{dz}\right)$ since as z increases, v decreases, when $z = r, v = 0$.

Putting the values, we get $P \times \pi z^2 = \eta \times 2\pi zl\left(-\dfrac{dv}{dz}\right)$ or, $dv = -\dfrac{P}{2\eta l} z dz$.

Integrating within limits, $\int_0^v dv = -\dfrac{P}{2\eta l}\int_r^z z dz$ or, $v = \dfrac{P}{4\eta l}\left(r^2 - z^2\right)$.

Now the total volume of the liquid flowing through the tube in unit time i.e. rate of liquid flow,

$$\frac{dV}{dt}=\int_0^r 2\pi z v dz=\int_0^r 2\pi z\times\frac{P}{4\eta l}\left(r^2-z^2\right)dz=\frac{\pi P}{2\eta l}\left[\frac{r^4}{2}-\frac{r^4}{4}\right]=\frac{\pi \mathrm{Pr}^4}{2\eta l}\left(\frac{1}{2}-\frac{1}{4}\right)=\frac{\pi P r^4}{8\eta l}.$$

Thus the Poiseuille equation for the rate of fluid (liquid or gas) flow , $\frac{dV}{dt}=\frac{\pi P r^4}{8\eta l}$ is derived.

Since the fluid flow is steady, hence $\frac{dV}{dt}=\frac{V}{t}$ i.e. V volume flowing in time t, so the equation is

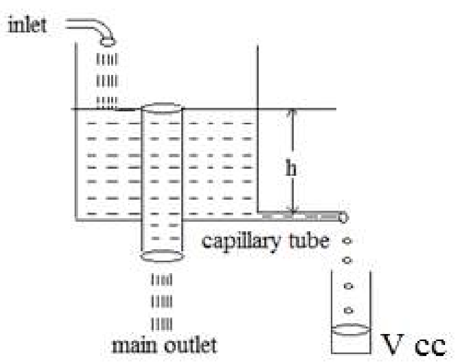
$\eta=\frac{\pi P r^4 t}{8lV}$. J L Poiseuille formulated the equation in 1844 from Newton's law of viscous flow.

This equation is applicable to incompressible fluid executing a streamlines flow in a tube.

Determination of viscosity coefficient (η) of a low viscous liquid:

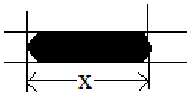
(i) Using Poiseuille equation directly. The Poiseuille equation is given as $\eta=\frac{\pi \mathrm{Pr}^4 t}{8lV}$ which is valid for laminar flow only.

Here V is the volume of liquid of viscosity coefficient (η) flowing in a capillary tube of radius r and length l under constant pressure difference, P in time t.



To determine η of a liquid, all the terms of the right hand side of the equation are to be determined.

The radius of the capillary (r) is determined by inserting a mercury pellet into the tube and the mass (m) and length (x) of the pellet are measured by using balance and travelling microscope. Using the relation, $m_{Hg}=\pi r^2 x\rho_{Hg}$, r can be calculated.



This method provides the absolute value of η of a liquid but the method is time consuming. Further a small error in the determination of r makes a large error in the value of viscosity coefficient, a r remains in the 4th power in the expression of η.

Problem: If there is 1% error in the value of r, the radius of the capillary, what will be the error in the viscosity coefficient value calculated using Poiseuille equation.

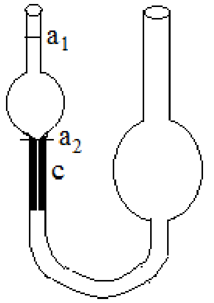
Solution: $\eta=\frac{\pi \mathrm{Pr}^4 t}{8lV}=k r^4$, where $k=\frac{\pi \mathrm{P} t}{8lV}$ so, $d\eta=4k r^3 dr$, or $\frac{d\eta}{\eta}=\frac{4k r^3 dr}{k r^4}$, or $\frac{d\eta}{\eta}=4\frac{dr}{r}$.

But the % of error in r = 1% i.e., $\frac{dr}{r}$ = 1 %, so $\frac{d\eta}{\eta}=4\%$ i.e., error in η = 4 %.

(ii) Using Oswald viscometer:

Easy way to determine the relative viscosity coefficient of a liquid with reference to water $\left(\eta_l/\eta_w\right)$ is done by using Ostwald viscometer.

This viscometer consists of two bulbs at different height as shown in the figure. The bulb in the wider tube is first filled with the liquid and then it is sucked up in the left hand limb up to level a_1. The liquid then flows down through the capillary (c) and time (t_l) required to fall from level a_1 to a_2 is carefully noted. The experiment is repeated with water in the same viscometer with same volume of the liquid by pipette. The corresponding time (t_w) is also noted.



Ostwald vicometer

Thus for liquid, the Poiseuille equation is

$$\eta_l = \frac{\pi h \rho_l g r^4 t_l}{8lV} \text{ and for water } \eta_w = \frac{\pi h \rho_w g r^4 t_w}{8lV}. \text{ So, } \frac{\eta_l}{\eta_w} = \frac{\rho_l\, t_l}{\rho_w\, t_w}$$

or, $\frac{\rho_l\, t_l}{\eta_l} = \frac{\rho_w\, t_w}{\eta_w}$ i.e. $\frac{\rho t}{\eta}$ is constant for a viscometer for all runs. So, $\eta_l = \eta_w \times \left({}^{\rho_l}\!/_{\rho_w} \right)\left({}^{t_l}\!/_{t_w} \right)$.

Density of the liquid (ρ_l) is determined by specific gravity bottle. Both t_l and t_w are noted by stopwatch. Density and viscosity coefficient of water are obtained from standard text book of physical chemistry.

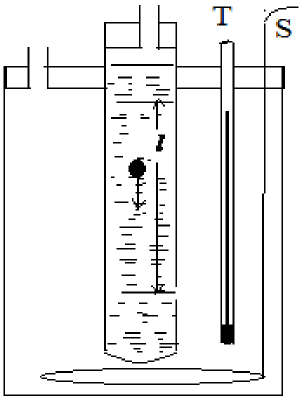
Precautions of the method: Temperature should be kept constant by using thermostat.
The capillary must be cleaned width chromic acid, water, etc before using.
The viscometer should be placed vertical and any sort of mechanical jerking must be avoided.

(iii) Using Stokes law: [Generally used for high viscous liquids]

When a metal ball of spherical in shape falls freely in a fluid, the viscous force develops that resists the fall of the ball. The layer of fluid, in contact with the ball moves with zero velocity (no-slip layer), a velocity gradient develops in the fluid surrounding the sphere. This gradient generates a viscous force, f_v resisting the sphere's motion. This viscous force is found to be proportional to the velocity of the ball (v) provided, v is not very high, $f_v = kv$, where k is called frictional constant. Stokes proved that for a solid sphere of radius, r moving at speed, v through a Newtonian fluid (the fluid that obeys Newton's law of viscous law) of viscosity, η the viscous force is

$$f_v = 6\pi\eta r v \qquad \text{This is called Stokes law.}$$

In this determination, liquid is generally taken in a tall cylinder and spherical metal ball is allowed to fall in the liquid. The driving force of the ball is due to gravitational force acting on the ball.



Falling sphere viscometer

$$f_d = \frac{4}{3}\pi r^3 \rho g, \qquad \text{where } \rho \text{ is the density of metal ball.}$$

This force is again is resisted by the buoyancy force and it results from the greater fluid pressure below the body than above it. This force is equal to the weight of volume of liquid that is replaced by the body.

$$f_{buoy} = \frac{4}{3}\pi r^3 \rho_l g, \qquad \text{where } \rho_l \text{ is the density of the liquid.}$$

When the driving force on the ball is equal to the opposing force, the ball falls with steady velocity.

$$f_d = f_{buoy} + f_v \quad \text{or,} \quad \frac{4}{3}\pi r^3 \rho g = \frac{4}{3}\pi r^3 \rho_l g + 6\pi\eta r v$$

or, $6\pi\eta rv=\frac{4}{3}\pi r^3\rho g-\frac{4}{3}\pi r^3\rho_l g$ or, $6\pi\eta rv=\frac{4}{3}\pi r^3\left(\rho-\rho_l\right)g$ or, $\eta=\frac{2}{9}\frac{r^2}{v}\left(\rho-\rho_l\right)g$

If the ball falls l distance in time t, then $v=\frac{l}{t}$ and so, $\eta=\frac{2}{9}\frac{r^2t}{l}\left(\rho-\rho_l\right)g$

Determination of all the terms of the RHS gives the absolute value of viscosity coefficient (η) of the liquid.

Relative viscosity: When water is taken as reference liquid and same ball is used to fall between the same two marks of l distance then ,

$\eta_l=\eta_w\times\left(\frac{t_l}{t_w}\right)\left(\frac{\rho-\rho_l}{\rho-\rho_w}\right)$ and η_w is obtained from the text book at the temperature of the experiment.

Problem: A steel ball of radius 2×10^{-3}m falls in a vertical column of castor oil. The coefficient of viscosity of castor oil is $0.7Nm^{-2}s$ and its density is $0.98\times10^3\ kg/m^3$. The density of the steel ball is $7.8\times10^3\ kg/m^3$ and $g=9.8ms^{-2}$. Find the terminal velocity of the steel ball.

[Burd. Univ. 2006]

Solution: $v=\frac{2}{9}\frac{r^2}{\eta}\left(\rho-\rho_l\right)g=\frac{2}{9}\frac{\left(2\times10^{-3}m\right)^2}{0.7Nm^{-2}s}\left(7.8-0.98\right)\times10^3\ kg/m^3\times9.8ms^{-2}$

$=\left(2\times4\times10^6\times6.82\times10^3\times9.8\right)/\left(9\times0.7\right)m/s=0.085\ m/s$

Temperature – dependence of viscosity coefficient of liquid

It is our common experience that viscosity varies with temperature. Honey, syrup, coal tar flow more rapidly when heated. Engine oil and hydraulic fluids thicken appreciably in winter season and significantly affect the performance of cars and other machinery.

Qualitative aspect of T-dependence: In general, viscosity of liquids decreases with rise of temperature.

As temperature increases, average speed of the molecules is increased resulting higher translational kinetic energy and this allows overcoming intermolecular attractions more easily.

Quantitative aspect of T- dependence: Dependence of η on T is quantitatively expressed as

$\eta=Ae^{E_v/RT}$, where E_v = activation energy of viscous flow and A is constant for the liquid. The above relation can be formulated as follows:

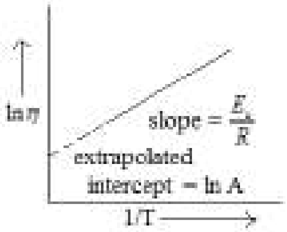
In order to move, a molecule in a liquid must escape from its equilibrium position so it needs a minimum energy. The probability that it can acquire at least energy E_v is proportional to $e^{-E_v/RT}$ (assuming two dimensional flow in layer). The mobility (fluidity) of the liquid should follow the Boltzmann energy distribution law and fluidity (φ) $\propto$ $e^{-E_v/RT}$. Since viscosity (η) is reciprocal to fluidity,

so $\eta\propto e^{E_v/RT}$ or, $\eta=Ae^{E_v/RT}$, where A is proportionality constant, characteristic property of the liquid. E_v is the activation energy of the viscous flow per mole and it is also the characteristic property of the liquid.

When $T\rightarrow0K$ or, $E_v=\infty$, $\eta\rightarrow\infty$, the liquid ceases to flow in either of the two cases.

Again, taking logarithm of both sides, we have $\ln\eta=\ln\text{A}+\frac{E_v}{R}\left(\frac{1}{T}\right)$.

Thus when $\ln\eta$ is plotted against $\left(1/T\right)$, a straight line is obtained from the slope of which E_v can be determined.



Again, $\ln \mathrm{A} = \ln\eta$, when $1/T \to 0$ i.e. $T \to \infty$.
However, in drawing the plot, problem is that data points obtained are very close for small range of 1/T.
So the slope and intercept obtained from the plot are liable to uncertainties.

The above equation in two temperatures gives $\ln\left(\frac{\eta_2}{\eta_1}\right) = \frac{E_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$.

This relation is also used to calculate E_v of a liquid.

Problem: The viscosities of water are 0.018 and 0.009 poise at 0^oC and 25^oC respectively. Calculate the average value of the viscous activation energy assuming it to be independent over this temperature range. [Burd. Univ.]

Solution: Putting the values in the relation, $\ln\left(\frac{\eta_2}{\eta_1}\right) = \frac{E_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$$\ln\left(\frac{0.018}{0.009}\right) = \frac{E_v}{2\,cal\,mol^{-1}K^{-1}}\left(\frac{1}{273} - \frac{1}{298}\right)K^{-1} \quad \text{or,} \quad \ln 2 = \frac{E_v}{2\,cal\,mol^{-1}}\left(\frac{25}{298\times273}\right)$$

$$E_v = \left(2\times298\times273\times\ln 2\right)/\,25\,cal\,mol^{-1} = 4511.22\,cal\,mol^{-1}$$

Pressure- dependence of viscosity of liquids:

The viscosity of a liquid is increased with the pressure over the liquid is increased. With increa**se** of pressure, number of holes is reduced and it is therefore more difficult for liquid to move. [Exception: water, its η decreases with increase of pressure over it.]

Addition of solutes:

Stronger the cohesive forces in a liquid, higher will be its viscosity. The factor that reduces cohesive forces, should lead to the decrease of viscosity of the liquid. Ionic salts reduce cohesive forces and hence in general it lowers the viscosity of the liquids.

Factors that increase η of a pure liquid:

Viscosity of a liquid is found to increase with the increase of molecular weight of the liquid and also with branching of the organic liquids.

Liquids having H-bonding have also high viscosity such as, glycerol, water, etc.

Determination of molar mass of a polymer:

Viscosity measurement of a polymer solution can be used to determine the molar mass of the polymer. When a polymer is dissolved in a suitable solvent, its viscosity (η) is increased. Let η and η_0 are the viscosity coefficients of the polymer solution of conc. c (gm/L) and pure solvent, then relative viscosity (η_r) = η/η_0 and specific viscosity (η_{sp}) = $\left(\eta-\eta_0\right)/\eta_0$.

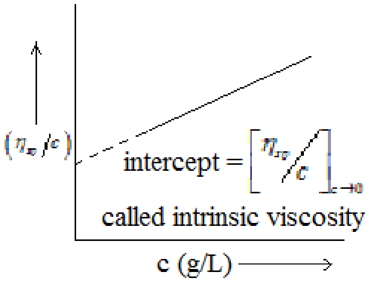
The reduced viscosity, $\eta_{red} = \eta_{sp}/c$. Thus the reduced viscosity (η_{red}) = $\left[\left(\eta-\eta_0\right)/\eta_0\right]/c$.

If reduced viscosity (η_{red}) is plotted against conc. (c), a straight line is obtained.

The extrapolated intercept is called intrinsic viscosity, $[\eta]$ which is $\left[\eta_{sp}/c\right]_{c\to 0}$. It may be called as the fractional change in the viscosity of a solution per unit conc. of polymer solution at infinite dilution.

This $[\eta]$ depends on the molar mass of the polymer. The empirical relation proposed by Flory is $[\eta] = \mathrm{K\,M}^{a}$

K and a are constants depending on the solvent, polymer-type and temperature of the solution.



If a = 1, M is weight average molar mass ($\bar{M}w$) of the polymer.

$$\left[\bar{M}w = \frac{w_1M_1 + w_2M_2 + w_3M_3 + \ldots\ldots..}{w_1 + w_2 + w_3 + \ldots\ldots\ldots\ldots\ldots.}\right] = \sum f_iM_i,$$

where w_1, w_2, w_3 are the weights of polymers having molar masses M_1, M_2, M_3, etc.

and f_i = weight fraction of the polymer of molar mass M_i.

When $a < 1$, M lies between $\bar{M}w$ and $\bar{M}_n$, and sometimes called viscosity average molar mass of the polymer. $\bar{M}_n$ = number average molar mass = $\dfrac{n_1M_1 + n_2M_2 + n_3M_3 + \ldots\ldots..}{n_1 + n_2 + n_3 + \ldots\ldots\ldots\ldots\ldots.}$ = $\sum x_iM_i$,

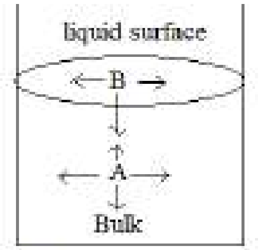
where x_i = mole fraction of the polymer of molar mass M_i.

Origin of the property:

Surface tension of a liquid is the surface property and it can be related to the intermolecular attraction present in the liquid.

Let us consider a molecule A in the bulk of the liquid. It is uniformly surrounded by other molecules and on an average it is attracted from all directions and the resultant force on it becomes nil. But the molecule B on the surface is partially surrounded by other molecules and experiences a resultant inward pull as a result of which, molecules on the surface try to leave the surface and enter into the bulk of the liquid. The liquid surface is under tension and tries to contract to get minimum surface area.

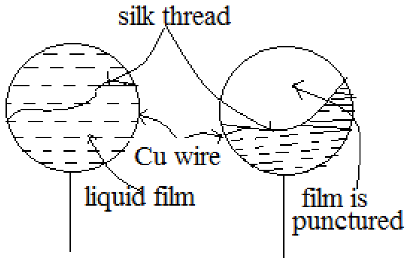
This unbalanced force of attraction on the surface molecules of a liquid is the origin of the property, **surface tension**. Higher the intermolecular attraction force (cohesive force), greater is the magnitude of surface tension of the liquid.



Forces on a molecule at the surface and in the bulk of the liquid

Demonstration of inward pull of silk thread:

Inward pull on surface molecules towards the bulk of the liquid can be demonstrated by the stretching of a silk thread in a liquid film of a circular wire when one side is punctured.



Consequences of surface tension of liquids:

Liquid assumes a shape that has a minimum surface area, because that enables the maximum number of molecules to remain in the bulk rather than on the surface of the liquid.

For this reason, droplet, when it falls freely, takes the spherical shape since this shape has surface/volume ratio minimum. If we drop some olive oil into a mixture of water and alcohol having same density as the oil, oil drops take spherical shape and float freely in the mixture. Lead shots are made by allowing molten lead to fall into a pool of water through a sieve at the top of the tower.

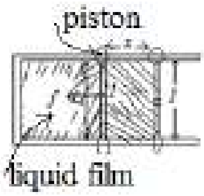
Other consequences of the property are the formation of bubbles of gas in a liquid, floating of needles on water surface, capillary-rise and capillary-fall of liquid, etc.

Definition of surface tension (γ) :

Since the surface is under tension, any attempt to make a penetration along any line on the surface will require an application of force to hold the separate portions of the surface together.

This force is called surface tension and is denoted by γ (gamma). It is expressed as force per unit length acting at right angles to the line along the surface of the liquid. Its unit is dyne/cm in CGS system and Nm^{-1} in SI system. The dimension of γ is MT^{-2}.

Stretching of a liquid film: The meaning of surface tension is better understood by the following experiment. The force, f required to stretch the film is found to be proportional to the length of the piston (l). Since there are two surfaces of the film, the total length of the film is $2l$. So $f \propto 2l$ or, $f = \gamma(2l)$.



The proportionality constant, γ is known as surface tension of the liquid and it can be looked upon as force exerted by a surface of unit length.

This increase of surface area of the liquid film against its natural tendency to contract will require performance of work.

The work required = $f_{opp} \times$displacement

i.e. $w = (\gamma \times 2l) \times x$ = $\gamma \times (2l \times x)$ = $\gamma \times \Delta A$ and so, $\gamma = w/\Delta A$.

So w is also the **surface energy** associated with the surface area, ΔA.

Thus the **surface tension (γ)** may also be defined as the work required to increase the surface of unit area. γ is equivalent with the surface energy per unit area though unit of latter is erg cm^{-2} or Jm^{-2} but both have the same dimension MT^{-2}.

Thermodynamics of the property:

Surface work is additional to PV-work so we regard it as a contribution to the Gibbs free energy of the system. The free energy change due to change in surface area (dA) of a liquid is given by

$dG = -SdT + Vdp + \gamma dA$ for one-component closed liquid system.

At constant T and P, $dG_{T,P} = \gamma dA$. For spontaneous process, $dG_{T,P} < 0$, and so $\mathrm{dA} < 0$.

This means that surfaces has natural tendency to contract as a system tends to attain smaller free energy (G), so it tends to acquire smaller surface area of the liquid.

Problem: A liquid drop of radius R and surface tension γ breaks up into n tiny droplets of equal size.

Show that the change in surface energy is given by $4\pi R^2\gamma(\mathrm{n}^{1/3} - 1)$. [Burd. Univ. 2008]

Solution: $\frac{4}{3}\pi R^3 = n \times \frac{4}{3}\pi r^3$ or, $R^3 = nr^3$ or, $R = n^{1/3}r$ or, $r = R/n^{1/3}$.

Increase of surface area = $n \times 4\pi r^2 - 4\pi R^2$ = $n \times 4\pi\left(R/n^{1/3}\right)^2 - 4\pi R^2$ = $4\pi R^2\left(\frac{n}{n^{2/3}} - 1\right)$

So increase of surface area = $4\pi R^2\left(n^{1/3} - 1\right)$ and increase of surface energy = $4\pi R^2\gamma\left(n^{1/3} - 1\right)$.

Problem: 1 cc of water is broken into droplets having a radius of 10^{-5} cm. Calculate the surface energy of the droplets relative to that of water. Given surface tension of water = 72.7 dyne/cm.

[Answer : 2.18×10^7 erg]

Wetting and non-wetting liquids:

Definition of angle of contact: Liquids can be classified into two types depending on their ability to wet the solid surface . Let us first define the angle of contact (θ) that measures the extent of wetting of the liquid. It is defined as the angle between the tangent to the liquid surface at the point of contact and the solid surface inside the liquid. Greater the angle of contact less is the wetting.

Difference of behaviors of wetting and non-wetting liquids:

Wetting liquid ($\theta < 90^o$)

For example : water on glass surface, ($\theta = 18^o$)

(1) Wetting liquid has tendency to spread on the solid surface.

(2) The liquid meniscus in the capillary tube is concave upwards and so there is rise of liquid

Non-wetting liquid ($\theta > 90^o$)

For example : mercury on glass surface ($\theta = 140^o$)

(1) Non-wetting liquid has a tendency to remain detached from the solid surface.

(2) The liquid meniscus is convex upwards and so there is fall of the liquid in the tube

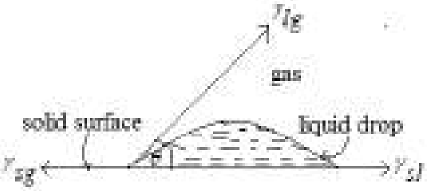
on the tube.	
(3) Intermolecular attraction between the liquid molecules (cohesion) is less than that between the liquid molecules and solid molecules (adhesion) i.e. cohesion < adhesion.	(3) Intermolecular attraction between the liquid molecules (cohesion) is greater than that liquid molecules and solid molecules (adhesion) i.e. cohesion > adhesion.

It is interesting to note that water cannot wet feather of birds so they can fly in the rain also. Water also cannot wet the leaves of lotus on the ponds.

Condition of wettability:

When a liquid drop remains stable of a solid surface, the following forces are balanced with themselves along the line of contact.

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta \quad \text{or,} \quad \cos\theta = \left(\gamma_{sg} - \gamma_{sl}\right)/\gamma_{lg}$$



(1) When the liquid wets the solid surface, $\theta < 90^o$ and $\cos\theta > 0$, so $\gamma_{sg} > \gamma_{sl}$ and the liquid spreads over the solid surface. That is, lower the interfacial tension γ_{sl}, smaller the value of θ and greater is the wettability of the liquid over the solid.

(2) When the liquid does not wet the solid surface, $\theta > 90^o$, $\cos\theta < 0$, so $\gamma_{sl} > \gamma_{sg}$. That is higher the interfacial tension $\left(\gamma_{sl}\right)$ between solid and liquid, less is the wettability of the liquid on the solid surface. The liquid does not spread more.

The equation does not hold if $\gamma_{sg} > \gamma_{sl} + \gamma_{\lg}$.

In that case, $\left(\gamma_{sg} - \gamma_{sl}\right) > \gamma_{lg}$ and $\cos\theta > 1$ which is not possible.

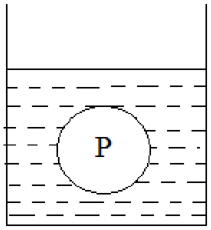
Again, when $\left(\gamma_{sg} - \gamma_{sl}\right) = \gamma_{lg}$, $\cos\theta = 1$ or, $\theta = 0^o$ i.e. solid is completely wet.

(3) Similarly, if $\gamma_{sl} > \left(\gamma_{sg} + \gamma_{lg}\right)$, then $\cos\theta < -1$, $\cos\theta > \cos 180^o$ or, $\theta > 180^o$ and liquid does not wet at all. The equation does not hold.

Excess pressure on the concave side of a bubble:

Difference among bubble, cavity and drop: Bubble is either a thin liquid film in which air and vapor are trapped or cavity that contains full of vapor in a liquid. Former has two surfaces while cavity has only one. The treatment of both is much the same, but factor 2 in the case of bubble is to be added. The drops are spheres of liquid in equilibrium with the vapor.

Bubble inside a liquid:



P = Excess pressure inside the bubble

Let a cavity inside a liquid of radius r is decreased to radius $r - dr$.

The surface energy is decreased $= -\gamma dA = -\gamma d\left(4\pi r^2\right) = -8\pi r\gamma dr$.

The amount of work done by the cavity to do so

$$= -P_{opp} \times dV = -Pd\left(\frac{4}{3}\pi r^3\right) = -P \times 4\pi r dr.$$

Equating the two we have $-P \times 4\pi r dr = -8\pi r\gamma dr$ or, $P_{excess} = 2\gamma/r$.

So the excess pressure inside the cavity (concave side) within the liquid is $P_{excess} = 2\gamma/r$.

When we consider the bubble suspended in air, $P_{excess} = 4\gamma/r$ since it has two surfaces.

Alternative formulation: The bubble inside the liquid remains in equilibrium (r remains time-invariant). This is due to the fact that the tendency to decrease their surface area is balanced by excess pressure inside. The cementing force that tends to decrease the surface area is for surface tension of the liquid forming the film and for the outward pressure, P_{out}. We know work required to stretch the surface of the bubble through radius dr is given by, $w = \gamma dA = \gamma \times d\left(4\pi r^2\right) = 8\pi r\gamma dr$. But work is force (opposing) × displacement. So the force opposing stretching through the distance, dr at the radius is $8\pi r\gamma$. Thus cementing force = $4\pi r^2 P_{out} + 8\pi r\gamma$. The disrupting force is due to the inward pressure, P_{in} and it is equal to $4\pi r^2 P_{in}$. Since the bubble is stable, these two forces are equal and so

$$4\pi r^2 P_{in} = 4\pi r^2 P_{out} + 8\pi r\gamma \text{ or, } 4\pi r^2 (P_{in} - P_{out}) = 8\pi r\gamma \text{ or, } P_{excess} = 2\gamma/r .$$

Excess pressure over plane surface: Thus we see that pressure inside a curved surface is always greater than the pressure outside, difference drops to zero as the radius of curvature tends to infinity (for flat surface). Since $P \propto 1/r$ for a liquid, smaller bubble requires higher pressure for its formation and maintenance. This is in agreement with our experience of blowing a balloon. It is difficult to blow initially but becomes easier as the size of the balloon increases.

The excess pressure is high as r is small. For example, P_{excess} in a bubble of radius 0.01 cm, P_{excess} = 14,600 dyne/cm^2 which is enough to sustain about 15 cm column of water.

$$[\, h = \frac{2\gamma}{\rho g r} = \frac{2 \times 72\, dyne\, cm^{-1}}{1 gm\, cm^{-3} \times 980\, cm\, \sec^{-2} \times 0.01 cm} = 14.7 cm \,].$$

Problem: A soap bubble is suspended in air with volume $\pi/6$ cc. Calculate the excess pressure inside the bubble if interfacial tension of soap solution and air is 27 dyne/cm.

Solution: $\frac{4}{3}\pi r^3 = \frac{\pi}{6} cm^3$ or, $r^3 = 8 cm^3$ or $r = 2$ cm. So, $P_{excess} = \frac{2\gamma}{r} = \frac{2 \times 27\, dyne\, cm^{-1}}{2 cm} = 27$ dyne/cm^2.

Problem: Two limbs of a vertical U-tube have internal diameters 0.5 mm and 0.3 mm respectively. It is partially filled with a liquid of density 0.3 gm/cc. The surface tension of the liquid is 60 dyne/cm. What is the difference in the levels of the liquid in the two limbs?

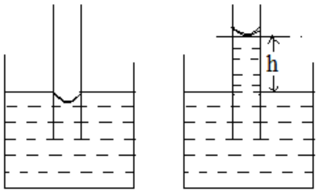
Solution: The difference of pressure between the two limbs, $\Delta P = \frac{2\gamma}{r} - \frac{2\gamma}{r'} = 2\gamma\left(\frac{1}{r} - \frac{1}{r'}\right)$

$$\text{or, } \Delta h \rho g = \Delta P = 2\gamma\left(\frac{1}{r} - \frac{1}{r'}\right) \text{ or, } \Delta h = \frac{2\gamma}{\rho g}\left(\frac{1}{r} - \frac{1}{r'}\right)$$

$$\text{or, } \Delta h = \frac{2 \times 60\, dyne\, cm^{-1}}{0.3\, gm\, cm^{-3} \times 981 cm\, \sec^{-2}}\left(\frac{1}{0.015 cm} - \frac{1}{0.025 cm}\right) = 10.87 cm$$

Explanation of capillary-rise and capillary-fall phenomena:

Capillary-rise for wetting liquid: When a glass capillary tube is immersed in water or any liquid that wets, there occurs a rise of liquid inside the capillary. It is called **capillary action.**



Before rising After rising

Explanation: The liquid wets the inner wall of the capillary and thereby surface area is increased. To decrease of surface area, the liquid must rise within the tube. As soon as this happens, however, the glass is again wet and again the liquid draws itself upwards. The process stops when the force of surface tension acting upwards becomes equal to the force due to column of liquid acting downwards.

$f_{up} = 2\pi r\gamma$ (approx. for wetting liquid) and $f_{down} = \pi r^2 h\rho g$.

The process stops when they are equal.

Equating, $2\pi r\gamma = \pi r^2 h\rho g$ or, $h = 2\gamma/(\rho g r)$ or, $\gamma = (\mathrm{h}\,\rho g r)/2$.

$hr = 2\gamma/(\rho g)$ = constant for a liquid at a given temperature.

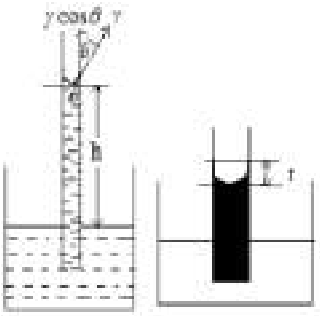
Thus, h vs. r plot is a rectangular hyperbola.

Capillary-fall for non-wetting liquid: In similar way, it can be shown that there will be capillary-fall for the liquid that does not wet the solid surface, such as mercury in glass tube.

The formulation also helps to determine the surface tension (γ) of a liquid.

Determination of Surface Tension of a Liquid:

(a) Capillary-rise method: Rise and fall of liquid in a capillary tube is due to surface tension. Let us take a wetting liquid and it rises in the capillary tube until the vertical component of the lifting force is balanced by the weight of the liquid in the capillary tube.



↑ Lifting force (upward force) = $2\pi r \times \gamma\cos\theta$, where r is radius of the tube and it is also the radius of the curvature of the liquid meniscus [$r = r_c/\cos\theta$ and $\cos\theta \approx 1$ for wetting liquid so $r \approx r_c$].

↓ The weight of the liquid (downward force) = $\pi r^2 h\rho g + v\rho g$,

where v is the volume of the liquid in the meniscus itself

= volume of the cylindrical tube of radius r and length r

– volume of empty hemisphere within the meniscus

= $\pi r^2 \times r - (1/2)\times(4/3)\pi r^3 = (1/3)\pi r^3$.

So the downward force = $\pi r^2 h\rho g + (1/3)\pi r^3 \rho g$ = $\pi r^2(\mathrm{h} + \frac{1}{3}\mathrm{r})\rho g$

At equilibrium, the two forces are equal, so $2\pi r \times \gamma\cos\theta = \pi r^2(\mathrm{h} + \frac{\mathrm{r}}{3})\rho g$ or, $\gamma = \frac{(h + r/3)\rho g r}{2\cos\theta}$.

For more accurate, ρ is sometimes replaced by $\rho_l - \rho_v$ thus, $\gamma = \frac{(h + r/3)(\rho_l - \rho_v) g r}{2\cos\theta}$.

However, for most wetting liquids, $\cos\theta \approx 1$ and $h >> r$, so $\gamma = (1/2)\mathrm{h}(\rho_l - \rho_v) g r$.

Problem: For water-air interface at 25^{o}C and 1 atm, calculate the rise in a capillary tube with inside diameter 0.2 mm. The surface tension of water at 25^{o}C is 72 dyne/cm. The density of air and water at 25^{o}C and 1 atm are 0.001g/cm^{-3} and 0.997 g/cm^{-3}. (g = 981 cm sec^{-2}).

Solution: $\gamma = \frac{1}{2} h\left(\rho_l - \rho_a\right) g\, r$ or, $h = \frac{2\gamma}{\left(\rho_l - \rho_a\right) g\, r} = \frac{2 \times 72 dyne/cm}{\left(0.997 - 0.001\right) g\, cm^{-3} \times 981 cm \sec^{-2} \times 0.01 cm}$

$= 14.74\, cm$.

Approximate working formula: Again, $\rho_l >> \rho_v$ and so for approximate measurement, working formula,

$$\gamma \ = \ \left(1/2\right) h \rho g r \ .$$

Since θ is not accurately determined, so this method does not give very accurate result.

For non-wetting liquids, h is depression of the liquid level in the capillary tube.

For determination of γ , h is determined by travelling microscope, ρ is determined by specific gravity bottle, r is determined by inserting a mercury-pellet and determining the mass of the pellet.

Precaution: Only precaution of the method is that the capillary must be well-cleaned and immersed vertically.

Relative surface tension: Relative surface tension of a liquid with reference to water using same capillary tube can be determined more easily.

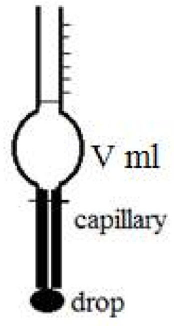
$$\gamma_l = \gamma_w \times \left(\rho_l / \rho_w\right) \times \left(h_l / h_w\right).$$

γ_w and ρ_w are obtained from the Text Book of Physical Chemistry at the temperature of the experiment

(b) Drop-weight or drop-number method:

Theory of the method: The liquid whose surface tension is to be measured is allowed to pass very slowly through a capillary (called stalagmometer) tip. The liquid falls as cylindrical drop at the mouth. Just at the point of detachment of the drop from the capillary tip, the upward force ($2\pi r \gamma$) is balanced by the downward force which consists of the weight (mg) of the drop and the excess pressure (γ / r) inside the cylindrical drop for its curved surface. Thus,

$$2\pi r \gamma = mg + \pi r^2 \times \frac{\gamma}{r} \quad \text{or,} \quad \gamma = \frac{mg}{\pi r}$$



(Stalagmometer)

Though the formulation is approximate, yet the relative value with respect to a reference liquid (usually water) works well.

$$\frac{\gamma_l}{\gamma_w} = \frac{m_l}{m_w} \quad \text{or,} \ \gamma_l = \gamma_w \times \frac{m_l}{m_w} \ .$$

Drop-number method: However this can be replaced by drop-number method. The number of drops obtained for the same volume, say V ml of the liquid and water are counted.

Thus, $$\frac{m_l}{m_w} = \frac{\left(V/n_l\right)\rho_l}{\left(V/n_w\right)\rho_w}, \quad \text{so} \quad \gamma_l = \gamma_w \times \left(\frac{\rho_l}{\rho_w}\right) \times \left(\frac{n_w}{n_l}\right).$$

Precautions: The liquid is allowed to drop slowly and stalagmometer must be cleaned. During the fall of the liquid, air current or mechanical jerking is avoided to get accurate result.

Effect of Temperature on Surface Tension:

γ decreases with rise of T and vanishes at T_c: As the temperature of a liquid, in equilibrium with its vapor, is raised, the phases becomes more and more alike. The number density of both the phases tends towards the same value. Inward pull on the surface molecules towards the bulk decreases, so the surface tension of the liquid is also decreased.

At the critical temperature, the liquid-vapor interface disappears and the surface tension of the liquid vanishes i.e., when $T = T_c$, $\gamma = 0$.

Eotvos equation: R. Von Eotvos found that molar surface energy $\left[k'(Mv)^{2/3}\gamma\right]$ varies linearly with temperature in degree celsius (t°C), assuming the molar volume of the liquid as spherical shape.

[Formulation of molar surface energy: Using spherical shape, the molar volume, $Mv = (4/3)\pi R^3$, where R = radius of the spherical mass and v the specific volume of the liquid, so $R = \left[\frac{3}{4\pi}(Mv)^{1/3}\right]$.

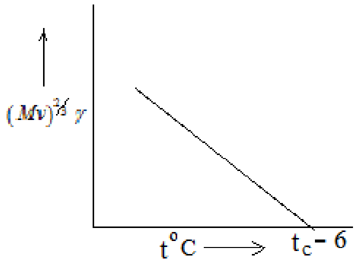
The molar surface area = $4\pi R^2 = 4\pi\left(\frac{3}{4\pi}\right)^{2/3}(Mv)^{2/3} = k'(Mv)^{2/3}$ and $k'(Mv)^{2/3}\gamma$ is the molar surface energy.]

Thus, Eotvos observation is $k'(Mv)^{2/3}\gamma = -k''t + c'$ or, $(Mv)^{2/3}\gamma = -k\,t + c$, where $k = k''/k'$.

When $t = t_c$, $\gamma = 0$, so $-k\,t_c + c = 0$ or, $c = k\,t_c$. Thus Eotvos relation is $(Mv)^{2/3}\gamma = k(t_c - t)$.

But Ramsay and Shield found that γ drops to zero approximately at $t_c - 6$. So the modified relation is

$$(Mv)^{2/3}\gamma = k(t_c - 6 - t).$$



Value of k: For normal and non-associated liquids, $k = 2.1$ when γ is measured in the cgs unit. For water, alcohol, carboxylic acid (associated liquids) k is less than 2.1 and k increases with temperature.

Empirical relation: When specific volume (v) is assumed to be temperature independent, then $(Mv)^{2/3}$ is constant. Again, if temperature is in Kelvin scale, the $t^oC = T - 273$ and $t_c = T_c - 273$, the empirical relation becomes $\gamma = k(T_c - T)$.

Problem: Surface tension of ethyl acetate ($T_c = 523K$) is 25 dyne/cm at 0°C. Find its value at 50°C.

Solution: $\gamma = k(T_c - T)$ or, $25\,dyne/cm = k(523 - 273)K$

or, $k = (25/250)\,dyne\,cm^{-1}K^{-1} = 0.1\,dyne\,cm^{-1}K^{-1}$,

so $\gamma = 0.1\,dyne\,cm^{-1}K^{-1}(523 - 323)K = 20\,dyne\,cm^{-1}$.

Vapor Pressure over a Curved Surface (Kelvin Equation)**:**

To derive the effect of curvature of liquid surface on vapor pressure, we may recall the expression of dG of a system that includes the change in surface area (dA) also.

$$dG = -SdT + VdP + \gamma dA + \Sigma\mu_i dn_i\ .$$

For one component (pure substance) open system, $dG = -SdT + VdP + \gamma dA + \mu dn$.

Last term (μdn) in the equation gives the change in G when dn moles of the substance are added to the system at constant T and P without changing the surface area of substance (planar surface).

So for planar surface, we can write $dG_{T,P,A} = \mu_{Planar}\, dn$

or, we can define chemical potential of the substance at constant T, P having planar surface

$$\mu_{Planar} = \left(\partial G/\partial n\right)_{T,P,A}.$$

It is the chemical potential of the component substance when it has planar surface at constant T and P. However, when dn moles of the substance are added to the spherical droplet, there occurs an increase of surface area (dA). [For a sphere, $dV = 4\pi r^2 dr$ and $dA = 8\pi r dr$, so $dA = 2\left(dV/r\right)$]

Thus, addition of dn moles of the substance increases the surface area,

$$dA = 2\frac{dV}{r} = 2\frac{\bar{V}dn}{r} = \left(2\frac{M}{\rho r}\right)dn,$$ where ρ is the density of the substance.

So the free energy change of a substance including surface area is given by

$$dG = -SdT + VdP + \left(2\frac{M}{\rho r}dn\right)\gamma + \mu_{planar}\, dn \quad \text{or,}\ dG = -SdT + VdP + \left(\frac{2M\gamma}{\rho r} + \mu_{planar}\right)dn\ .$$

At constant T and P, free energy change of the substance, $dG_{T,P} = \left(\dfrac{2M\gamma}{\rho r} + \mu_{planar}\right)dn$

Thus the chemical potential of the substance (liquid) when it is in droplet (convex curved surface)

$$\mu_{drop} = \left(\frac{\partial G}{\partial n}\right)_{T,P} \qquad \text{or,} \qquad \mu_{drop} = \left(\frac{2M\gamma}{\rho r} + \mu_{planar}\right)\ .$$

Now, $\mu_{drop} - \mu_{planar} = \dfrac{2M\gamma}{\rho r}$, but $\mu_{drop} - \mu_{planar} = RT\ln\dfrac{p}{p_0}$ [vapor obeys ideally]

It is the change in chemical potential of the substance when 1 mole is transferred from planar surface (vapor pressure, p_0) to the droplet (vapor pressure, p). Therefore,

$$RT\ln\frac{p}{p_0} = \frac{2M\gamma}{\rho r} \quad \text{or,}\ \ln\frac{p}{p_0} = \frac{2\gamma}{\rho r}\frac{M}{RT} \quad \text{(Kelvin equation)}$$

Since all the terms in the RHS are (+ve), so $p > p_0$ i.e., vapor over a drop (convex surface) is greater than the planar (flat) surface. Smaller the radius of curvature, higher will be p than p_0.

The vapor pressure of water as a function of radius of curvature of the surface is shown below at 25°C,

$r(cm)$	p/p_0	$r(cm)$	p/p_0
10^{-4}	1.001	10^{-6}	1.111,
10^{-5}	1.011	10^{-7}	2.88

p_0 = 23.75 mm at 25°C

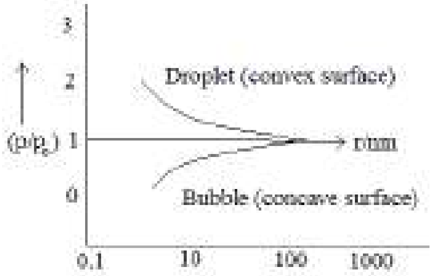
But when the liquid is transferred to the concave surface, the surface area is decreased and free energy change due to surface tension is $dG = -\gamma dA$. The Kelvin equation becomes

$$\text{or,}\quad \ln\frac{p}{p_0} = -\frac{2\gamma}{\rho r}.\frac{M}{RT}\text{, so}\quad \ln\frac{p}{p_0} = (-\text{ve})\quad\text{and}\quad p < p_0.$$

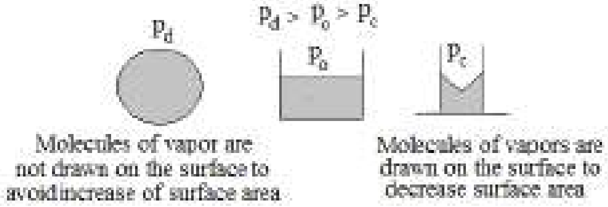
That is, vapor pressure of the concave surface of a wetting liquid in a glass capillary tube or in small bubble is less than that of the flat surface of the liquid.

The figure shows that vapor pressure of a small droplet exceeds that of plane surface of the liquid, and vapor pressure of a concave surface of a liquid is less than that of a plane surface. It is assumed that surface tension does not depend on the radius of curvature of the surface.

This is obvious that small droplets are having vapor pressure higher than the bulk liquid because molecules are not drawn into the interior by so many near neighbors.



And concave surface of a wetting liquid in a capillary has lower vapor pressure than the bulk liquid because the molecules are drawn into the interior by more neighbors than in a flat surface.



The consequence of the equation is that higher vapor pressure is required to condense vapors into small droplets as dew drops. Similarly, liquids have a tendency to superheat (boiling delayed) at their boiling points. If a small bubble starts to form at the boiling point, the equation is not satisfied. The bubble will be squeezed out of existence by the force of surface tension. There occurs then bumping. At a temperature above the boiling point, vapor pressure will be enough high and the bubble of certain radius will be thermodynamically stable. The liquid will be superheated in absence of foreign substance.

Problem: Calculate the vapor pressure inside the bubble of water vapor and outside a drop of water, in each case taking the radius as 10 nm. At 298K, the surface tension of water is 72 dyne/cm and the vapor pressure over a flat surface is 23.76 mm of Hg.

Solution: In the Kelvin equation,

$$\frac{2\gamma}{\rho r}.\frac{M}{RT} = \frac{2\times 72\,dyne\,cm^{-1}}{1gm\,cm^{-3}\times 10^{-7}\,cm}\times\frac{18gm\,mol^{-1}}{8.31\times 10^{7}\,erg\,mol^{-1}K^{-1}\times 298K} = 0.1046.$$

For drop of water, $\ln p/p_0 = 0.1046$ or, $p/p_0 = 1.11$ and vapor pressure, $p = 1.11\times 23.76$ mm of Hg.

So the vapor pressure of water over drop of water, $p = 26.37$ mm of Hg

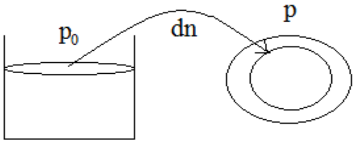
Again for bubble, $\ln p/p_0 = -0.1046$ or, $p/p_0 = 0.901$ and $p = 0.901\times 23.76$ mm of Hg

So the vapor pressure inside the bubble of water, $p = 26.37$ mm of Hg.

Problem: Calculate the vapor pressure of a water droplet at 25°C of radius $2.0\times 10^{-9}m$. The vapor pressure of a flat surface of water-air interface at 25°C is 0.072 N m^{-1}. Density of water at 25°C is given as 10^3 Kg m^{-3}. **[Answer: 5344.59 Pa]**

Alternative derivation of Kelvin equation:

Let dn mole of the liquid is transferred from flat surface having vapor pressure p_0 to the spherical droplet at vapor pressure p. The free energy change for this transfer is given by



$$dG = dn\,RT\ln\left(p/p_0\right).$$

For this transfer, there occurs increase of surface area of the drop by dA.

The flat surface has no change of surface area due to this transfer. So the increase of free energy due to this increase of surface area is

$$dG = \gamma dA,$$

(while other controlling factors for the free energy change remain fixed)

Equating the two, we have $dn\,RT\ln\left(p/p_0\right) = \gamma dA$. But, $dA = dV \times \frac{2}{r} = \left(\frac{M}{\rho} \times \frac{2}{r}\right)dn$.

So, $dn\,RT\ln\left(p/p_0\right) = \gamma\left(\frac{M}{\rho} \times \frac{2}{r}\right)dn$ or, $RT\ln\left(p/p_0\right) = \gamma\left(\frac{M}{\rho} \times \frac{2}{r}\right)$ or, $\ln\left(p/p_0\right) = \frac{2\gamma}{\rho r} \times \frac{M}{RT}$.

For transfer to the concave surface, there occurs decrease of surface area and $dG = -\gamma dA$.

The Kelvin equation in such case will be $\ln\left(p/p_0\right) = -\frac{2\gamma}{\rho r} \times \frac{M}{RT}$.

PROPERTIES OF SOLIDS

Introduction:

A substance can remain in three states – gas, liquid and solid. But solids differ from liquids and gases by their high density and low compressibility. Solids have definite shape, mechanical strength and rigidity. This is due to close proximity of molecules in solids and hence high attractive forces.

Classifications:

Solids are classified generally into crystal and amorphous. The crystals have flat surfaces, sharp edges and pointed corners, arranged symmetrically.

Crystals have definite melting point at a definite pressure.

Complete ordered arrangement of constituent particles (atoms, molecules or ions) in the crystal gives definite geometric shape.

The crystals have definite melting point at a definite pressure.

Anisotropicity of the crystals

Crystalline solids (other than belonging to cubic class) are anisotropic. Magnitude of some properties depends on the directions along which it is measured. Refractive index, thermal and electrical conductivities, coefficient of thermal expansion are of such properties.

For example, refractive index ($\mu = \sin i / \sin r$) of $AgNO_3$ crystal at 20^{o}C along X, Y and Z axes are 1.73, 1.74 and 1.79 respectively for Na D-light ($\lambda = 5890 \; and \; 5896$ Å).

In a crystal of AgI, the coefficient of thermal expansion is observed to be (+)ve in one direction and (-)ve in other direction.

This directional nature of the properties (anisotropicity arises due to different fixed arrangement in different directions.

Origin of the anisotropicity in the crystal

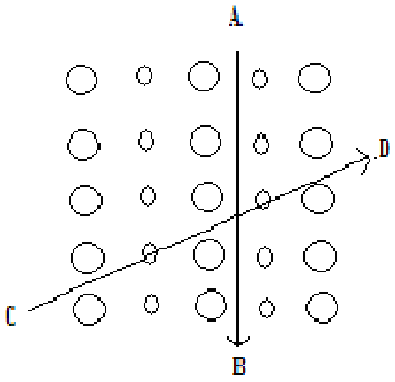


Fig. Arrangement of particles is different in different directions so the value of some physical properties is found to be different in different directions. Anisotropic nature of the property develops in the crystal.

Isotropicity of the amorphous substances

On the other hand, amorphous (Greek word, amorphos meaning no form) solids though they have definite shape, hardness and rigidity, but have no sharp melting point. They melt (soften) over a range of temperature and they can be moulded or blown into various shapes.

These amorphous solids are isotropic and the properties do not vary with the directions along which it is measured. Glass, pitch, rubber, plastics belong to this class.

The isotropy- nature of the amorphous solids originates due to the lack of ordered structure of the constituent particles (random arrangement).

One striking example is that quartz is a crystalline structure while quartz glass is amorphous having no long range order arrangement.

In many ways, amorphous solids closely resemble to liquids and thereby called 'super-cooled liquids'. Like liquids, they have tendency to flow though very slowly due to high viscosity. Glass panes fixed to windows and doors of old buildings are invariably found to be slightly

thicker at the bottom than at the top. This is, because the glass flows down very slowly and makes the bottom slightly thicker.
Hence forth by solid, we always mean the crystalline substance and not amorphous substance.

Crystalline solids:

Thermodynamics of formation of a crystal

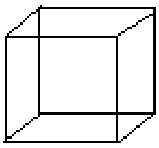
Highly ordered arrangement of constituent particles is accompanied by a lowering of internal energy of system. We have combined equation of 1st and 2nd law of thermodynamics as,

$$dU = TdS - PdV$$

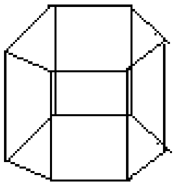
For this order arrangement, the entropy (S) is minimum and the volume (V) is maximum. This makes the internal energy of the system (U) minimum.

Crystals are bound by flat surface or face (f), sharp edges (e) and pointed corners (c). Two faces when intersect, edge is developed, and when two edges meet, a corner is formed. These external features of a crystal are related as,

$$f + c = e + 2.$$



Cube
(f = 6, c = 8 and e = 12)



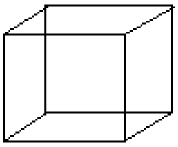
Hexagonal
(f = 8, c = 12 and e = 18)

First law of crystallography:

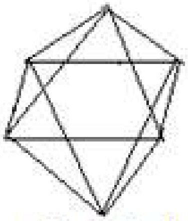
The size and shape of a crystal depend on the conditions under which crystal grows. If the rate of deposition is slow, a big size crystal is formed, each face has got sufficient time for its proper development.

Again, if some impurity is present in the solution from which the crystal is formed, the shape may be different. For example, NaCl crystallizes as cubes from aqueous solution while as octahedral from 15% urea solution.

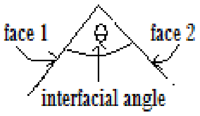
One substance can take different crystalline shapes



Cube



Octahedral



The angle between two faces is the interfacial angle. Interfacial angle is the angle between the normal to the two intersecting faces. This angle is measured by the instrument, called Goniometer developed in 1780.
The first quantitative measurements on crystals were made by Niel Stensen, professor of Anatomy at Copenhagen in 1669. He measured the angles between the corresponding faces of quartz crystals of different shapes and stated the first law of crystallography.

"The angles between the corresponding faces of various crystals of the same substance are same".
Interfacial angle is thus a characteristic property of a solid in spite of its different possible crystalline geometric shapes.

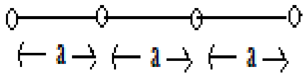
Crystal lattice and unit cell:

The internal regularity of the particles reminds the idea of lattice. The 3-dimensional ordered structure is called space lattice.

One-dimensional lattice point

Due to difficulty in representing the constituent particles in the crystal lattice, points are used instead of particles. The centre of mass of the particle represents the point in the lattice. Thus the arrangement of points in 3-dimensions gives point lattice.

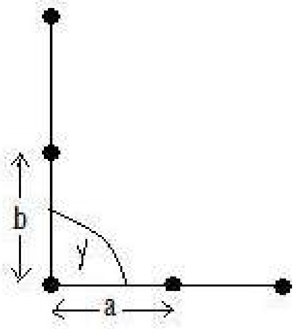
When the points are arranged in one line regularly at a certain fixed distance, it is called one-dimensional lattice.

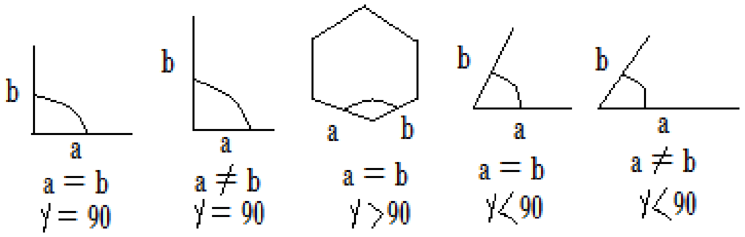


The spacing of the points is fixed and is equal to 'a', called distance lattice parameter.

When the set of points are repeated regularly on a plane (along two co-ordinate axes), it is called two-dimensional lattice. The points in two-dimensional lattice plane can be arranged in five and only five different ways on the basis of lattice parameters a , b and γ.

The points in 2-d lattice can be arranged only in 5 different



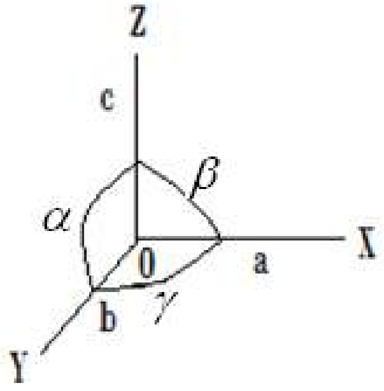


Six cell pparameters are required to describe a 3-d lattice.

Six parameters are required to define the 3-d lattice , three distance parameters, a, b, c and three angle parameters, α, β, γ.

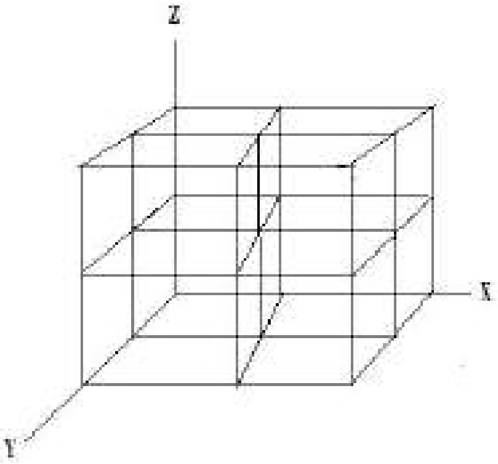
The angle parameters are

$\angle XOY = \gamma, \angle XOZ = \beta$ and $\angle YOZ = \alpha$



One unit cell retains all the characteristics of the crystal

If similar points are connected by sets of parallel lines along the co-ordinate axes, the space will be divided into a large number of small symmetrical units. These basic units of the space lattice are known as 'unit cells'. This unit cell is the smallest building unit of the crystal. Like molecule in a substance, unit cell retains all the characteristic features of the crystal. Any point placed in one unit cell must occupy the same relative position in every unit cell of the crystal.



Symmetry in crystals:

Symmetry operations are used to compare the extent of symmetry of different crystals

Symmetry is a kind of regularity in the arrangement of the constituent particles in a crystal. Symmetry of a crystal is described in terms of certain symmetry operations which transform a spatial arrangement into an arrangement that is virtually indistinguishable from the original one. The crystals can be classified into seven crystal systems according to their symmetry operations. How much a crystal is symmetrical, that can be measured by the number of symmetry operations (elements of symmetry). Greater the number of elements of symmetry of the crystal, greater is its symmetry.

Generally the three types of symmetry operations are used to describe the symmetry of a crystal. These are discussed below.

(a) Axis of symmetry:

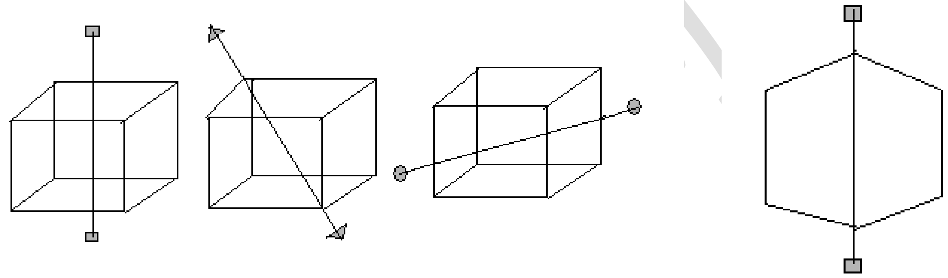
An axis of symmetry is an imaginary line passing through the centre of the crystal about which if the crystal is rotated through an angle of 360^o, the crystal takes a number of indistinguishable configurations with the original one. This rotation operation is denoted by C_n, where n is the number of such indistinguishable configurations that appears.

If two such equivalent arrangements will occur in a complete rotation, i.e. through 360^0, the axis is said to be a twofold (diad) axis of symmetry (C_2).

If the complete rotation leads to the three same result as the original one, the axis is called a threefold (traid) axis of symmetry (C_3).

In the cubic crystal, there are three C_4 axes of symmetry passing through the opposite faces, four C_3 axes of symmetry passing through the opposite corners of the cube and six C_2 axes of symmetry emerging from the opposite edges.

A cubic crystal has 13 axis of symmetry.

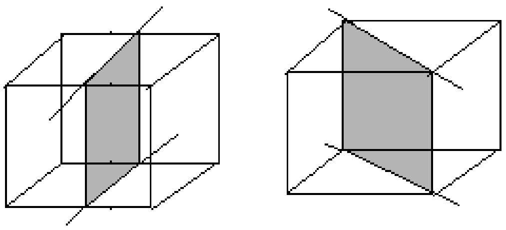


(b) Plane of symmetry:

A crystal is said to possess a plane of symmetry if it can be divided by an imaginary plane into two parts such that one is the exact *mirror image* of the other. The plane of symmetry is usually designated by σ. When the mirror plane is perpendicular to the direction of the principal axis (axis of highest order), it is called *horizontal mirror plane* and is denoted by σ_h. On the other hand, when a mirror plane contains the principal axis of symmetry, it is known as the *vertical mirror plane* and is denoted by σ_v.

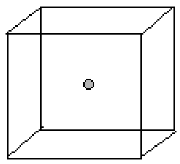
A cubic crystal has 9 plane of symmetry.

In the cubic crystal, there are three principal planes and six diagonal planes of symmetry. Thus the cubic crystal contains total nine planes of symmetry.



(c) Centre of symmetry:

It is denoted by i. Centre of symmetry of a crystal is a point such that any line drawn through it intersects the surface of the crystal at equal distances in both the directions. A crystal can have only one centre of symmetry. Thus a cubic crystal has one centre of symmetry.



Crystal systems:

With distance cell parameters a, b, c and three angle cell parameters α, β, γ, it is possible to have seven crystal systems of different geometrical shapes. These are given bellow:

Crystal systems	Cell parameters	Elements of symmetry	Examples
1. Cubic	a = b = c, $\alpha = \beta = \gamma = 90^o$	13 axial, 9 plane	NaCl. KCl
2. Tetragonal	$a = b \neq c$, $\alpha = \beta = \gamma = 90^o$	5 axial, 5 plane	Rhombic S,
3. Orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^o$	3 axial, 3 plane	White tin, TiO_2
4. Rhombohedral	a = b = c, $\alpha = \beta = \gamma \neq 90^o$	7 axial, 7 plane	Calcite
5. Hexagonal	$a = b \neq c$, $\alpha = \beta = 90^o$, $\gamma = 120^o$	----- do ------	Graphite, Mg
6. Monoclinic	$a \neq b \neq c$, $\alpha = \beta = 90^o$, $\beta \neq 90^o$	1 axial, 1 plane	Monoclinic S
7. Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^o$	No axial, No plane	$K_2Cr_2O_7$

Any other geometrical shape with these six cell parameters gives rise to one that have the same elements of symmetry with the one of the above seven crystal systems.

Out of these seven crystal systems, cubic system has maximum elements of symmetry – 13 axis of symmetry ($3C_4$, at right angles to each other, $4C_3$, axes passing through the opposite corners and $6C_2$, axes emerging from opposite edges), 9 plane of symmetry (3 are principal planes and 6 are diagonal planes) and one centre of symmetry.

3rd law of crystallography

On the basis of symmetry, 3rd law of crystallography is stated as,

"all the crystals of the same substance have the same elements of symmetry."

Out of the seven crystal systems, three are having orthogonal axes ($\alpha = \beta = \gamma = 90^o$) and these are cubic system, tetragonal system and orthorhombic system.

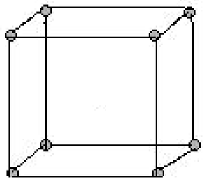
Type of crystal system can be identified from external features the crystal

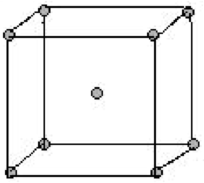
Examination of the macroscopic shape of a single crystal helps to find the crystal system it belongs to and allow 'a', 'b' and 'c' axes to be located. With the use of the instrument, called Goniometer, it is possible to find the angle parameters, α, β, γ.

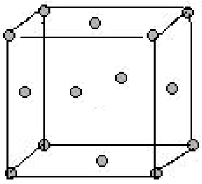
These external features of the crystal help to determine the crystal system but it can not tell us the internal arrangement of the constituent particles in the crystal.

Bravais class of the crystal systems:

Bravais (1848) showed that considering the position of the lattice points in the different crystal systems a total of 14 different Bravais classes are possible. These are discussed below:


Simple cubic crystal
(P)


Bodi-centred cubic crystal
(I)


Face-cubic crystal
(F)

Three Bravais classes in cubic system.

1. Cubic crystal system:

a = b = c,

$\alpha = \beta = \gamma = 90^o$

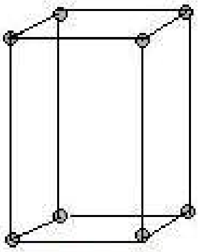
It has got three Bravais classes.

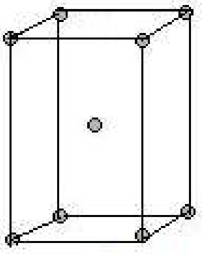
2. Tetragonal crystal system:

a = b ≠ c, $\alpha = \beta = \gamma = 90^o$

Two Bravais classes in tetragonal crystal system.

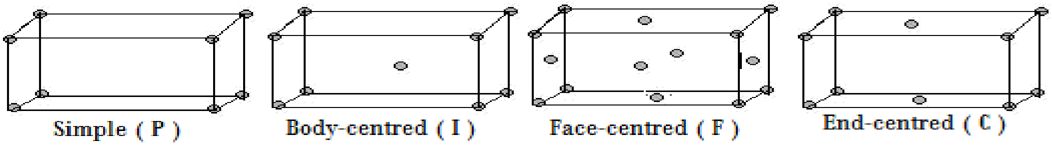
It has got two Bravais classes. One is simple (P) and other is end-centred (C) in which the lattice points are on the opposite faces bound by a and b axes.


Simple (P)


Body-centred (I)

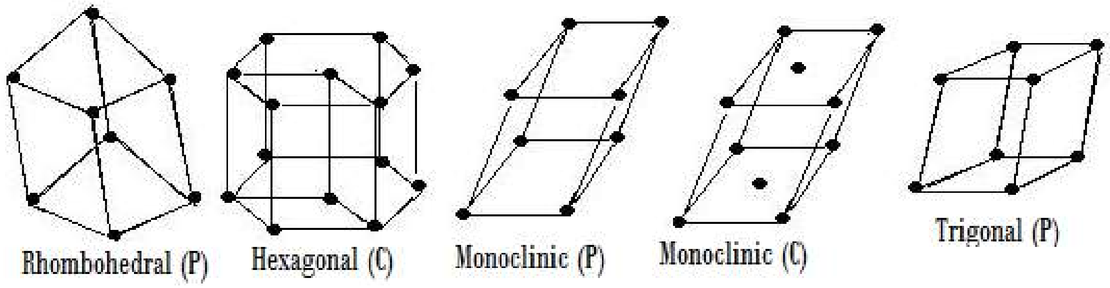
Four Bravais classes in orthorhombic crystal system.

3. Orthorhombic crystal system: $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^o$. It has four Bravais classes.


Simple (P) Body-centred (I) Face-centred (F) End-centred (C)

Monoclinic has two Bravais classes and others have one in each crystal system

4. Rhombohedral crystal system ($a = b = c$, $\alpha = \beta = \gamma \neq 90^o$) has only one simple (P) Bravais class.
5. Hexagonal crystal system ($a = b \neq c$, $\alpha = \beta = 90^o$, $\gamma = 120^o$) has only one simple (P) Bravais class.
6. Monoclinic crystal system ($a \neq b \neq c$), $\alpha = \gamma = 90^o$, $\beta = 90^o$) has two Bravais classes – simple (P) and end-centred(C).
7. Triclinic crystal system ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^o$) has only one simple (P) Bravais class arrangement.


Rhombohedral (P) Hexagonal (C) Monoclinic (P) Monoclinic (C) Trigonal (P)

BU 2005. Q1(b)

How many crystal systems and Bravais lattice are there in crystalline solids? (1)

BU, 2006, Q4(c)(ii)

Show that two dimensional lattice with five fold rotation axis of symmetry is not possible. (5)

Ans. : See Physical Chemistry Vol. I by K L Kapoor, Page 126.

Assignment of lattice points per unit cell in a cubic system:

Cubic crystal system has three Bravais classes.

Primitive cubic crystal has one lattice point per unit cell.

1. Primitive cubic system (P):
   It has 8 points at the 8 corners of the cube so each point at the corner is equally shared by eight other adjacent unit cells.
   Hence contribution of each atom to the unit cell is (1/8).

$$\text{Total number of lattice points per unit cell} = 8 \times \frac{1}{8} = 1$$

bcc has two lattice points per unit cell.

2. Body-centred cubic system (I):
   The lattice points occupy each corner of the cube along with one point at the centre of the cube. The body- centre point belongs exclusively to the unit cell.

$$\text{Total number of lattice points per unit (bcc) cell} = 8 \times \frac{1}{8} + 1 = 2.$$

fcc has four lattice points per unit cell.

3. Face-centred cubic system (F);
   The lattice points occupy each corner of the cube along with at the centre of each face of the cube. The face-centred point is equally shared by two adjacent unit cells.
   Such type of points is six at the centre of six faces of the cube lattice.

$$\text{Total number of lattice points per unit (fcc) cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4.$$

Density of cubic system:

Density of a solid can be accurately determined from the experiments and its value can also be used to unit cell dimensions. Again if the cell dimension is determined by Bragg's diffractometer, the type of Bravais class of the crystal can be ascertained.

Density of the solid helps to suggest the type of Bravais class of the crystal

For the cube unit cell, the volume = a^3, where a is the edge-length.

Mass of the unit cell = $\left(\frac{M}{N_A}\right)\times n$ where, M = molar mass of the solid and

n = number of the constituent particles per unit cell..

It is one for primitive (P), two for bcc and four for fcc.

So the density of the solid

$$\rho = \frac{M\times n}{N_A\times a^3}$$

For tetragonal crystalline solid, $\rho = \frac{M\times n}{N_A\times a^2 b}$, and for orthorhombic solid, $\rho = \frac{M\times n}{N_A\times abc}$.

a, b and c are the distance cell parameters of the orthorhombic crystalline solid.

Problems:

(1) K has a cubic lattice and at 25°C the density of K is 0.856 gm/cc and X-ray diffraction shows the unit cell edge length is 5.33Å. Find the number of formula units in a unit cell of K . What kind of cubic lattice does K have? [Physical Chemistry – Ira Lavine]

(Answer → n = 2 and bcc)

(2) Copper crystallises in the fcc pattern. From X-ray diffraction study, the edge length of the unit cell has been found to be 0.360 nm. If the density of copper is 8.94×10^3 Kg m^{-3}, calculate the Avogadro number N_A. [C U, 96]

(Answer – 6.095×10^{23} mol^{-1})

(3) The orthorhombic crystallised form of an organic compound contains 2 molecules per unit cell with cell dimensions 12.05, 15.05 and 2.69 Å and density of the crystal is 1.419 gm/cc. What will be the molar mass of the organic compound?

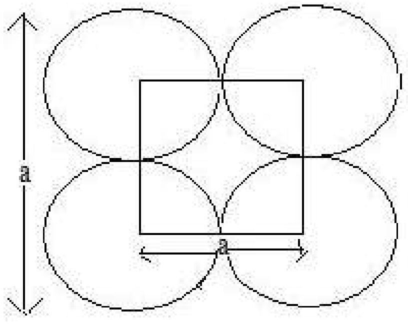
(Answer – 208.47) [Civil Service Exam, 1999]

Packing in cubic lattice :

For the calculation of packing of the constituent particles in the crystal, we consider that each particle is (a) rigid sphere, (b) identical with other constituents and (c) they are touching each other in the unit cell.

Assumptions for calculation of packing fraction in the crystal.

(1) Simple cubic cell:



In this simple cubic cell, spheres are at the corners and they are touching along the side of the unit cell. Thus the distance between the centres of two spheres = a and radius of each sphere = a/2.

The volume of each sphere = $\frac{4}{3}\pi\left(\frac{a}{2}\right)^3$.

Volume of the unit cell = a^3

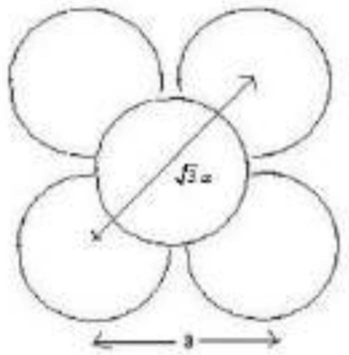
Thus the fraction of the total volume of unit cell occupied by the sphere

Simple cubic crystal is 52.3% packed

$$= \frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = 0.523 = 52.3\%$$ and the void volume = 47.7%.

The structure is relatively open since only 52.3% of the space is occupied by the constituent particles and the rest 47.7% remains empty.

(2) Body-centred cubic cell:



bcc is 68% packed

Besides the eight corners of the cube, one sphere occupies at the centre position.
The body-centred cube contains two spheres.
The spheres are touching along the body-diagonal of the cube which is equal to

$$\sqrt{(face\,diagonal)^2+(edgelength)^2}=\sqrt{3}\,a$$

Thus 4r = $\sqrt{3}\,a$ or, r = $\frac{\sqrt{3}\,a}{4}$.

The fraction of the total volume of the unit cell occupied by the spheres = $\dfrac{2\times\frac{4}{3}\pi\left(\frac{\sqrt{3}\,a}{4}\right)^3}{a^3}$ = 0.68.

So the volume occupied = 68% and void space = 32%.
In this arrangement, each sphere has eight nearest neighbours and thus the co-ordination number (equidistant nearest neighbour) = 8.
About 22 elements crystallise with bcc. In this cubic crystal, the constituents do not occupy the highest fraction of space so these are very soft. Alkali metals have this bcc.

Soft elements like alkali metals have this structure. Co-ordination number = 8

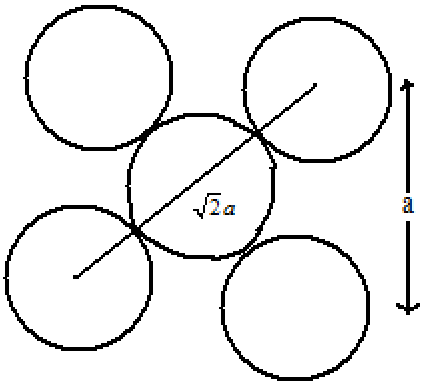
In the crystals of elements all the constituent particles are atoms and same. But there are compounds with body-centred lattice, the particle at the centre is different from that at the corners. Caesium chloride (CsCl) is such an example. In its unit cube, corners are occupied by the Cl^- ions and Cs^+ ion is at the centre or vice versa. In fact it may be regarded as a case of two simple cube lattices (one of Cl^- ions and one of Cs^+ ions) interpenetrating.
Caesium chloride has a body-centred cubic lattice. Find the number of Cs^+ and Cl^- ions per unit cell. (2)

BU,2006, Q 2(a)

(3) Face-centred cubic cell :

In this Bravais class of cubic system, besides eight corners of the cube, six spheres occupy at the centre of each face. The cell contains total 4 spheres and the spheres are touching each other along the face diagonal.

Thus, 4r = $\sqrt{2}\,a$, so r = $a/2\sqrt{2}$.



The fraction of the total volume of the unit cell occupied by the 4 spheres

fcc is 74% packed

= $\dfrac{4\times\frac{4}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3}{a^3}$ = 0.74. So the packing = 74%, and void space = 26%.

Thus, in general, the packing fraction (fraction of volume occupied) is independent of the radius of the sphere and depend only on the nature of the Bravais class of crystal system. This packing is more common for uniform spheres and is indeed closest packing possible in cubic system. Thus it follows that the density of substances increases from simple to bcc to fcc.
Most metals are either face-centred or hexagonal. Many elements such as the solidified inert gases, or metals like Cu, Ag, Au, Ni etc possess this type of structure.

Sodium chloride (NaCl) crystal has this type structure and two fcc units one of Na^+ ions and other of Cl^- ions are interpenetrating.

The co-ordination number (equidistant nearest neighbours) is 12 in both face-centred cube and hexagonal structure.

Problem:

(1) Al crystallises in a cubic closed packed structure. Its metallic radius is 125 pm.

(i) What is the length of the side of the unit cell?

(ii) How many unit cells are there in 1.00 cm^3 of Al?

[Answer: $a = 3.54 \times 10^{-8}$ cm, number of unit cell = 2.25×10^{22}].

(2) Gold crystallizes in fcc lattice. The atomic weight and density of gold are 196.97 and 19.4 gm/cc respectively. The length of the unit cell is

(a) 2.563 Å (b) 3.230 Å (c) 4.070 Å (d) 8.140 Å [GATE] [Ans. (c)]

(3) Sodium metal crystallizes in the body-centred cubic lattice with cell edge a.

The radius of the sodium atom is

(a) $a/\sqrt{2}$ (b) $a\sqrt{3}/2$ (c) $a\sqrt{3}/4$ (d) $a/2\sqrt{2}$ [GATE] {Ans. (c)}

Crystal cleavage and development of its faces :

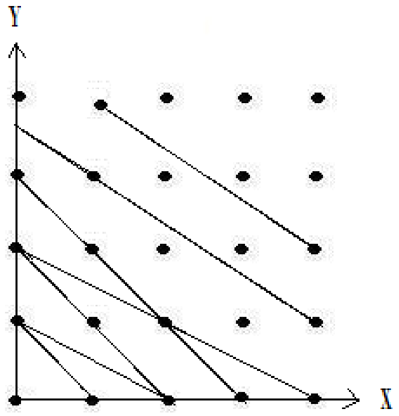
A series of large number of parallel and equidistant planes, called lattice planes can be drawn through the lattice points.

Greater point density plane forms the face of the crystal.

Among these large number of planes, only few planes represent the faces of the crystal.

Only those planes that have large point density can form the crystal faces. Greater the point density of a plane, greater is the probability of that plane to form the crystal face. Planes passing through the crystallographic axes have highest density of points, so these planes generally form the crystal faces.

Thus, natural fractures of a crystal will contain the planes parallel to these faces so the cleavage planes would correspond to the naturally developed crystal faces.



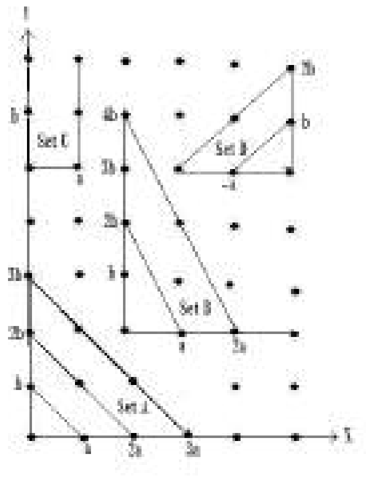
It can also be shown that the planes with the highest density are also planes with largest distance of separation (d) so that interatomic attraction between the planes would be minimum.

Lattice planes and their designations :

A plane is indexed in terms of the intercepts it makes with the axes.

Let us consider the set of parallel and equidistant planes (set A, set B, set C and set D). These sets of planes make intercept with the crystallographic axes X and Y (passing through maximum lattice points) and parallel to the Z-axis.

The designation of the planes is expressed in terms of the intercepts they make with the crystallographic axes. The orientation of the planes are useful to discuss the structure of crystals



(i.e. arrangement of lattice points in space within the crystal). The unit intercepts with X-and Y-axes are ‘a’ & ‘b’.

Set A planes: Consisting of 3 planes which are parallel & equidistant. The intercepts of the 1st plane = a, b, ∞, the intercepts of the 2nd plane= $2a, 2b, \infty$ and the intercepts of the 3rd plane = $3a, 3b, \infty$. Since the plane is parallel to Z-axis & hence it cuts Z-axis at ∞.

The ratio of the intercepts for the set A planes $a : b : \infty$ = same for all three parallel equidistant planes under set A. Similarly, the intercept-ratio of

set B planes = $a : 2b : \infty$,

set C planes have intercept-ratio = $a : \infty : \infty$ and

set D planes have intercept-ratio = $-a : b : \infty$

This shows that any plane can be designated in terms of the intercept-ratio with the crystallographic axes, and all the planes under a given set (which are parallel & equidistant) can be named by the same intercept-ratio. This can be better understood by the Hauy's laws of rational intercepts or indices.

Law of rational indices: The law states that the intercepts of any plane of a crystal, with crystallographic axes, are either equal to the unit intercepts (i.e. intercepts made by unit plane, which are denoted by a, b, c) or some small whole number multiples of them. Such a ratio of three intercepts of any plane is given by pa: qb: and rc where p, q, r are small whole numbers and a, b, c are the intercepts made by the unit plane with the crystallographic axes.

Intercepts of any plane along the axes are either the unit intercepts or small whole number multiples of them.

This law also means that all planes cut a given axis at distance from the origin that bears a simple ratio to one another.

These coefficients, p, q, r are called Weiss indices of the plane & these members characterise and represent any plane of the crystal. The corresponding plane is designated as (p q r) plane. Usually the Weiss indices are small whole members but in some cases they may be fraction & infinity.

The numbers in the Weiss indices are replaced by Miller indices (h k l).

W.H. Miller introduced (h k l) for indexing the planes & they are obtained by the following way.

The Miller indices of a plane are obtained by the reciprocals of Weiss indices (i.e. the coefficients of unit intercepts a, b, c) & when it is found necessary, the reciprocals are to be multiplied by smallest number (i.e. least common multiple, LCM) to make all reciprocals as simple small integers.

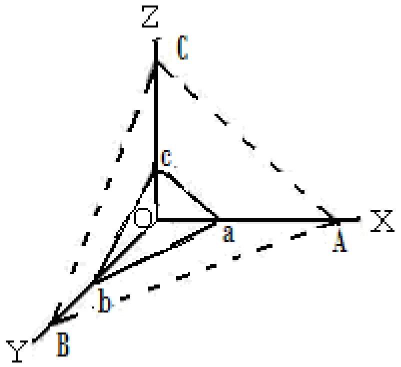
Thus, the sets of planes under discussion are designated as

Set A: intercept ratio→ a : b : ∞, Weiss indices → (11∞), Miller Indices (110)

Set B: intercept ratio→ a : 2b : ∞ Weiss indices (12∞), Miller indices (210)

Set C: intercept ratio→ a : $\infty : \infty$, Weiss indices → ($1\infty\ \infty$), Miller indices (100)

Set D: intercept ratio→ $-$ a : b : ∞ , Weiss indices → (-11∞), Miller indices $(\bar{1}10)$.



Let OX, OY & OZ represent three crystallographic axes and ABC is one plane that cuts the crystallographic axes at A, B and C. Thus OA, OB and OC are the intercepts along the axes. Thus according to the law, OA = pa, OB = qb, OC = rc where the of the unit intercepts of the unit planes are a, b, c.

The Miller indices (h k l) are defined as

$$h=\frac{1}{p}=\frac{a}{OA},\quad k=\frac{1}{q}=\frac{b}{OB}\ \text{ and } l=\frac{1}{r}=\frac{c}{OC}.$$

$$h=\frac{a}{\text{intercept of the plane along } X-axis},\quad k=\frac{b}{\text{intercept of the plane along } Y-axis}$$

$$l=\frac{c}{\text{intercept of the plane along } Z-axis}.$$

So, larger the value of Miller indices, smaller is the intercept made by the plane.
Thus (222) plane has intercepts which are one-half of those of (111) planes. However both the planes are parallel and equivalent.

Problem: The planes in a crystalline solid intersect the crystal axes at (2a, b, c), (-a, b, c), (a, 2b,3c), (3a,2b,c) and (-a, b,∝). Find the Miller indices of the planes.

Answer: (122), $(\bar{1}\,11)$, (632), (236), $(\bar{1}\,10)$.

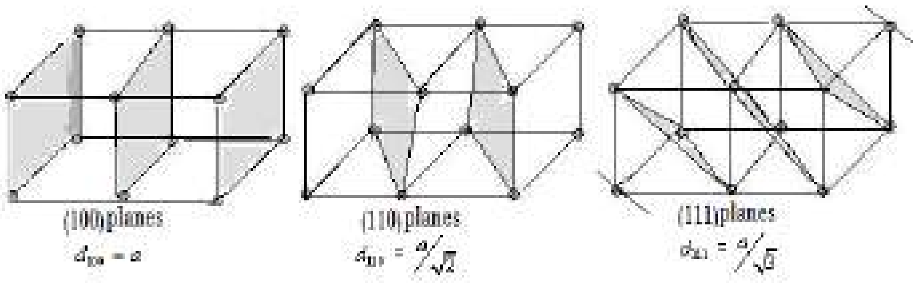
Lattice planes in cubic system :

Three type of planes are possible in cubic crystal.

The planes are defined by Miller indices (hkl) and Miller indices do not define merely a particular plane but define a set of parallel and equidistant planes. It is the ratio of the Miller indices which are important for the planes. For examples, the (222) plane is the same as (111) plane, the (200) plane is same as (100) plane. Only the interplanar distances are different. The (200) planes have half interplanar distance of the (100) planes.

(a) Simple cubic crystal: [Lattice points occupy the eight corners of the cube.]

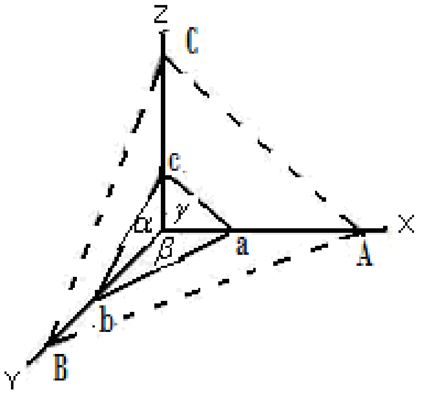
Let ‘a’ is the edge length of the cubic cell and d is interplanar distance. One plane is passing through the origin.


(100)planes $d_{100}=a$
(110)planes $d_{110}=a/\sqrt{2}$
(111)planes $d_{111}=a/\sqrt{3}$

Interplanar ratio in simple cubic class.

The ratio of the interplanar distances are given as:

$$d_{100}:d_{110}:d_{111}=a:\frac{a}{\sqrt{2}}:\frac{a}{\sqrt{3}}=1:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}}=1:0.707:0.577\,.$$

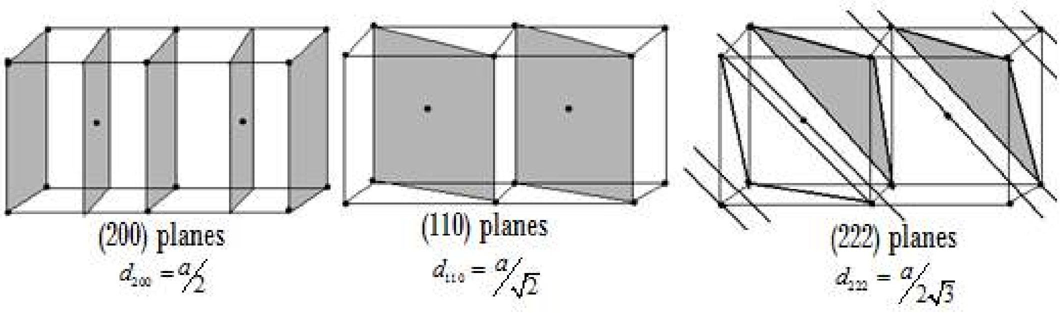


crystallographic axes.
Thus according to the law where the intercepts of the unit plane are a, b, c.
OA = pa, OB = qb, OC = rc.
The Miller indices (h k l) are defined as

$$h=\frac{1}{p}=\frac{a}{OA},\quad k=\frac{1}{q}=\frac{b}{OB}\ \text{ and } l=\frac{1}{r}=\frac{c}{OC}.$$

Larger the value of Miller indices, smaller is the intercepts.

(b) Body-centred cubic crystal: [The lattice points occupy the centre of the cube in addition to the eight corners.]



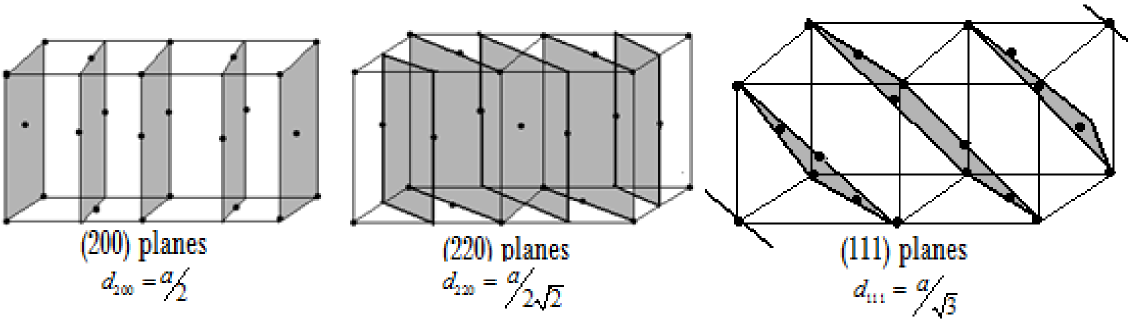
(200) planes $d_{200} = a/2$ (110) planes $d_{110} = a/\sqrt{2}$ (222) planes $d_{222} = a/2\sqrt{3}$

The interplanar ratio of the three planes is given as:

Interplanar ratio of bcc

$$d_{200} : d_{110} : d_{222} = \frac{a}{2} : \frac{a}{\sqrt{2}} : \frac{a}{2\sqrt{3}} = 1 : \sqrt{2} : \frac{1}{\sqrt{3}} = 1 : 1.414 : 0.577 .$$

(c) Face-centred cubic crystal : [The lattice points occupy the centre of six faces in addition to the eight corners of the cube.]



(200) planes $d_{200} = a/2$ (220) planes $d_{220} = a/2\sqrt{2}$ (111) planes $d_{111} = a/\sqrt{3}$

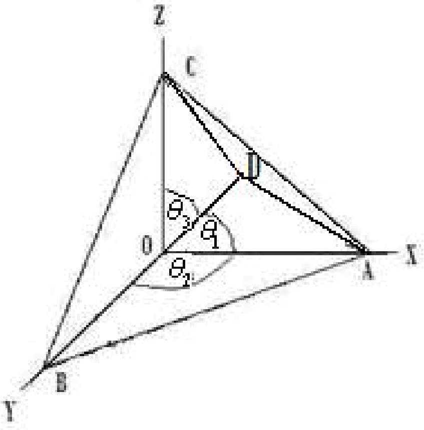
Interplanar ratio of fcc.

$$d_{200} : d_{220} : d_{111} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.707 : 1.154 \quad .$$

The interplanar distance (d_{hkl}) of a crystal is determined by Bragg X-ray diffraction measurements. This helps to find out the Bravais class to which a crystal system belongs.

Expression for calculation of interplanar distance (d_{hkl}) :

The crystal systems belonging to the orthogonal axes (having a set of perpendicular axes) are cubic, tetragonal and orthorhombic. For these crystal systems, the interplanar distance can be calculated by the use of certain formula.
Miller indices that define the set of parallel planes, taking one of which passes through the origin. If a perpendicular is drawn from the origin to the nearest plane of Miller indices (hkl), then the perpendicular distance, represented by d_{hkl} becomes the interplanar spacing between the planes indexed by (hkl).



If θ_1, θ_2 *and* θ_3 are the angles which this perpendicular makes with the three axes, then

$$d_{hkl} = OA\cos\theta_1 = \frac{a}{h}\cos\theta_1$$

$$d_{hkl} = OB\cos\theta_2 = \frac{b}{k}\cos\theta_2 \text{ and } d_{hkl} = OC\cos\theta_3 = \frac{c}{l}\cos\theta_3 .$$

Interplanar distance of hkl planes in terms of unit distance parameters in crystals having orthogonal axes.

Therefore, $\cos\theta_1 = \left(\frac{h}{a}\right)d_{hkl}$, $\cos\theta_2 = \left(\frac{k}{b}\right)d_{hkl}$ and $\cos\theta_3 = \left(\frac{l}{c}\right)d_{hkl}$.

Since , cos θ_1 , cos θ_2 and cos θ_3 are the direction cosines of the perpendicular line, so

$$\cos^2\theta_1 + \cos^2\theta_2 + \cos^2\theta_3 = 1 \qquad \text{or,} \qquad \left(\frac{h^2}{a^2}\right)d_{hkl}^2 + \left(\frac{k^2}{b^2}\right)d_{hkl}^2 + \left(\frac{l^2}{c^2}\right)d_{hkl}^2 = 1.$$

So, $\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$. This relation is applicable to any crystal having orthogonal axes.

For cubic system, a = b = c, hence $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2}$ or, $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$.

For tetragonal crystal system, a = b $\neq$ c, $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$.

For orthorhombic system, $a \neq b \neq c$, $\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$.

It can be shown that $\frac{1}{d_{nhnknl}^2} = n^2\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)$ or, $\frac{1}{d_{nhnknl}^2} = n^2 \times \frac{1}{d_{hkl}^2}$.

Problem : Calculate the separation of (a) the (123) planes and (b) the (246) planes of an orthorhombic unit cell with a = 0.17 nm, b = 0.93 nm and c = 0.75 nm.

Solution : $d_{123} = 0.13\ nm$ *and* $d_{246} = 0.065\,nm$. [Civil Service Exam. 2003]

Some regions of electromagnetic radiation :

Electromagnetic radiation is generally classified into several regions depending on the wave length. It is given below:

Classification of light into regions on the basis of wave length range.

Name of the regions	Wave length range
Cosmic rays	$10^{-4}A \to 10^{-2}A$
γ – rays	$10^{-2}A \to 10^{-1}A$
X - rays	$10^{-1}A \to 50A$
Vacuum UV	$50A \to 2500A$
UV	$2500A \to 4000A$
Visible	$4000A \to 8000A$
I R	$8000A \to 1,25,000A$
Far I R	$1.25\times10^{5}A \to 10^{6}A$
Microwave	$10^{-2}cm \to 3\,cm$
Radio wave	$3\,cm \to 300\,cm$

Diffraction of electromagnetic radiation :

Wave length and amplitude of electromagnetic radiation.

Electromagnetic radiation consists of a wave that propagates in space with the velocity of light. The wave is characterised by frequency (ν) or by wave length (λ) and amplitude (displacement of the wave in a direction perpendicular to the direction of its propagation).

The frequency (ν) and wave length (λ) of the light are related as

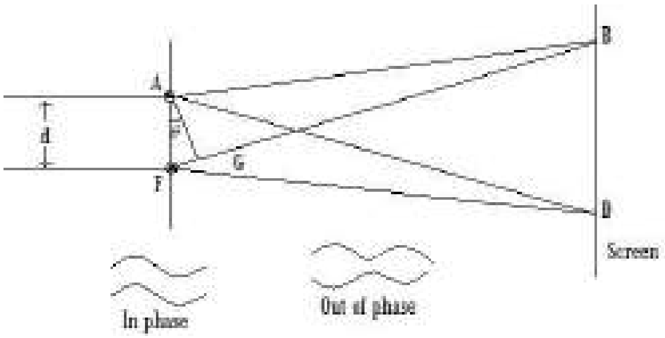
$$\nu = \frac{c}{\lambda}, \text{ where c is the velocity of the light.}$$

Two waves of same wave length and amplitude from two different sources reinforce each other when their maxima and minima coincide. These results as constructive interference and forms as bright point (B) on the screen placed to the path of the rays (in phase).

Diffraction of two light rays of same frequency and amplitude

On the other hands, they may interfere and exactly cancel each other when their maxima and minima do not coincide (out of phase).

This is destructive interference and appears as dark point (D) on the screen.



Condition of two light rays for being in phase giving constructive interference

These interference phenomena form the basis of diffraction of light by diffraction grating.

The diffraction grating consists of a transparent medium (such as glass) on which are ruled a large number of very fine, equidistant parallel opaque lines. When a light ray from a monochromatic source is incident perpendicular on the grating, all the clear spaces will emit light waves in all directions radially outwards. The wave length and amplitude of the diffracted light rays are same as the incident light rays. The waves from two apertures will cross at some point beyond the grating. If the screen is placed at this crossing point, a series of bright and dark spots will be observed on the screen.

Condition of bright spot is that when both the waves are in phase and for that, extra distance travelled by one of the waves must be an integral multiple of wave length (λ) of light

i.e. $FG = n\lambda$, where n = 1,2,3, etc.

but, $FG = d \sin\theta$ so $d \sin\theta = n\lambda$.

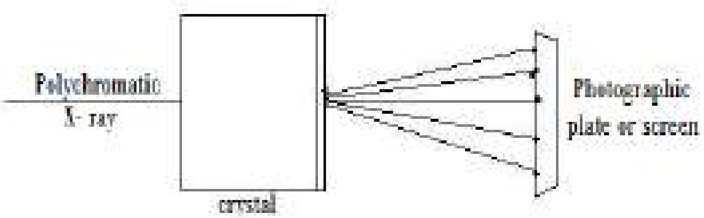
For the two waves forming bright spot, $d \sin\theta = n\lambda$.

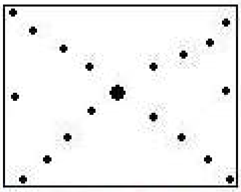
Thus, maximum value of λ = d, since maximum value of $\sin\theta$ = 1 and minimum value of n = 1. For crystal planes, $d \approx 10^{-8}$ cm so the maximum wave length of the light used for diffraction from crystal planes is also about 10^{-8} cm. This light falls in the region of X- rays. Thus, X-rays and not UV light is used for the diffraction by crystal planes.

Diffraction of X-rays by crystal :

In 1912, Max Von Laue predicted that since the distances between the particles in a crystal are of same order of magnitude ($\approx 10^{-8}\ cm$) as the wave length of X-rays, the former could be used as three dimensional transmission grating. He also obtained a diffraction pattern when a beam of polychromatic X-rays was passed through the crystal.

Laue experiment with polychromatic X-ray and 3-D transmission crystal grating.





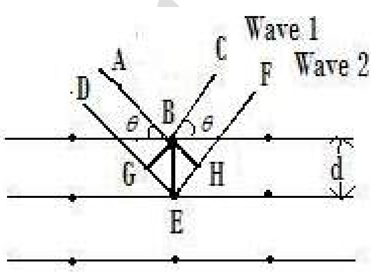
Laue diffraction pattern

Bragg 's diffraction equation : ($2d\sin\theta = n\lambda$).

Bragg's experiment with monochromatic X-rays.

B H Bragg and W L Bragg employed a crystal not only as a transmission grating as in the Laue method, but also a reflection grating. The series of equally spaced lattice planes will serve as grating. As the interplanar spacing (d) is comparable with the wave length (λ) of X-rays, latter is diffracted by crystal planes.

When X-rays are incident on a crystal face, they penetrate into the crystal and suffer reflections on striking the constituent particles in successive planes.



Path difference of two X-rays must be integral multiple of λ for the rays

If the reflected waves from successive layers are out of phase then due to destructive interference, no diffraction will be observed. If, however, the reflected waves are in phase, then due to constructive interference, a diffraction bright spot will be observed. The condition for a reflection to give constructive interference is that the path difference between the two waves must be integral multiple of wavelength of light.

Let θ be the incident angle of a monochromatic X-rays of wavelength (λ) with the parallel equidistant planes of particles of interplanar spacing d. The waves are in phase before striking the planes. Two such waves labelled as wave 1 and wave 2 are shown. After reflection, two waves will be in phase provided the extra distance travelled by wave 2 is an integral multiple of λ .

The extra distance can be obtained by dropping perpendiculars BG and BH from B to wave2.

Therefore, AB = DG and BC = HF. Again, GE = HE = d sinθ.

Thus , the extra distance = GE + HE = 2 d sinθ.

In order to wave 1 and wave 2 are in phase, the condition to be satisfied as,

$$2\,d\sin\theta = n\lambda$$

where, n = 1,2,3, etc and is called order of reflections.

Critical discussion on Bragg 's equation ($2\,d\sin\theta = n\lambda$ **) :**

Minimum value of n is 1 and max^{m}. value is such that nλ must not exceed 2d

(1) Restriction of the value of n : n is called order of reflection and it is equal to the number of wave lengths in the path-difference between waves reflected by adjacent planes. n cannot take the value zero in such case two rays are same as path-difference becomes zero.

n can take only integral values with limitation that sinθ must not exceed one, in such case, nλ must not be greater than 2d.

(2) Again, $\sin\theta = n\left(\lambda/2d\right)$. This shows that the crystal planes cannot produce reflection at any angles but at those discrete angles such that $\sin\theta$ becomes integral multiple of $\left(\lambda/2d\right)$. Thus, we have more than one reflection at angles θ_1, θ_2 ... corresponding to the values of n = 1, 2, -- respectively for fixed values of λ and d. The equation shows that higher order reflections will occur at larger values of $\sin\theta$, and hence at larger angles.

For max^m. reflection of two rays, sinθ must be integral multiple of $\left(\lambda/2d\right)$

Experimentally it is found that lower order reflections are more intense and intensities of higher order reflection drop off rapidly.

(3) In dealing with X-rays diffraction, it is customary to express higher order reflections in terms of the first order reflection from planes of higher (hkl). The equation is

$2\, d_{hkl} \sin\theta = n\lambda$, where d_{hkl} = interplanar distance of (hkl) planes.

Higher order reflections can be expressed by the 1st order reflection from planes of higher (hkl).

But we have seen that $\frac{d_{hkl}}{n} = d_{nh\,nk\,nl}$.

Now, rearranging the Bragg's equation, we get, $2\,\frac{d_{hkl}}{n}\sin\theta = \lambda$ or, $2\,d_{nh\,nk\,nl}\sin\theta = \lambda$.

This means that a second order reflection (n = 2) from (111) planes may be considered to be equivalent to the first order reflection from (222) planes. Similarly, a third order reflection from (100) planes is equivalent to first order reflection from (300) planes.

(4) Maximum value of λ : Bragg's equation is $\lambda = \frac{2d\sin\theta}{n}$. So for max^n. value of λ,

$$\lambda_{\max} = 2d\,\frac{(\sin\theta)_{\max}}{n_{\min}}, \quad \text{but } (\sin\theta)_{\max} = 1 \text{ and } n_{\min} = 1. \quad \text{Hence,} \quad \boxed{\lambda_{\max} = 2\text{d.}}$$

This means that the wave length of light used for Bragg's diffraction must not exceed twice the interplanar spacing of the crystal studied. This shows that since d $\approx$ 1A, thus λ is of 10^{-8} cm range. so X-rays and not UV light is required for crystallographic studies. When, $\lambda \rangle 2d$, $\sin\theta \rangle \frac{n\lambda}{2d} \rangle 1$ and there will be no diffraction.

Wave length of X-rays used must not exceed twice of interplanar distance of the crystal.

Similarly, $d_{\min} = \lambda/2$, that is in order to obtain diffraction pattern, the lattice planes in the crystal should have a separation of $\lambda/2$ or greater.

(5) Diffraction from different sets of planes:

So far, we have considered the reflection of X-rays from identical sets of planes i.e.. the planes that contains identical constituent particles of having same particle density.

For reflection from two different sets of planes, let us consider that one set is represented by AA and BB and other set by $A'A'$, $B'B'$ of interplanar distance d.

Condition of two reflected rays to be in phase from two different set of planes.

If x is the distance between AA and $A'A'$ or between BB and $B'B'$ and $n\lambda$ is the path difference for the rays from AA and BB planes then for the same angles of incidence θ, the path-difference for the rays reflected from AA and $A'A'$ or BB and $B'B'$ is $xn\lambda/d$.

If this is also an integral multiple of wave length then the rays reflected from AA and BB planes will be reinforced by the rays from $A'A'$ and $B'B'$ planes and a strong reflection maxima will be obtained.

However, if $x = d/2$, $xn\lambda/d = n\lambda/2$

So, when n = 2, 4, 6 (i.e. n = even numbers), the reflection beam will be in phase and strong reflection occurs between the planes AA and $A'A'$.

For n = 1, 3, 5, (i.e. n = odd numbers), the reflection will be in opposition, reflection beam will be less intense.

It means that one identical set of planes are interposed at the midway of the other identical planes, then 2nd and 4th order reflections are more intense and 1st and 3rd order reflection intensity will be less.

Planes of high particle density produce better reflection of X-rays.

Planes of high particles density produce better scattering of X-rays which gives a more intense beam. If more than one kind of particles is present in the crystal, the particle with greater number of electrons has greater scattering power for light elements. Between Na^+ and Cl^- ions, latter ions have more scattering power while K^+ and Cl^- have same scattering power as both the ions are iso-electronic.

Similarly, from X-rays diffraction, it is not possible to distinguish between atoms which differ only by the possession of one addition electron, such as nitrogen and carbon.

The scattering power of H-atom is very small and over-shadowed by the effect of neighbouring atoms containing large number of electrons and is not deduced by X-ray method.

problem: (i)Derive Bragg's equation to show that $2\,d\sin\theta = n\lambda$ for the reflection of X-rays from the faces of the crystal.

(ii) Calculate the interplanar spacing (d-spacing) in a cubic crystal of the second order refection from such planes are obtained $\sin\theta = 0.38$, when X-rays of $\lambda = 154$ pm are used. [IAS' 2010, m = 20]

Solution: (i) See the text note.

(ii) $d = \dfrac{n\lambda}{2\sin\theta} = \dfrac{2\times 154\ pm}{2\times 0.38} = 405.3\ pm$.

Experimental set-up of Bragg 's diffractometer : ($2\,d\sin\theta = n\lambda$**)**

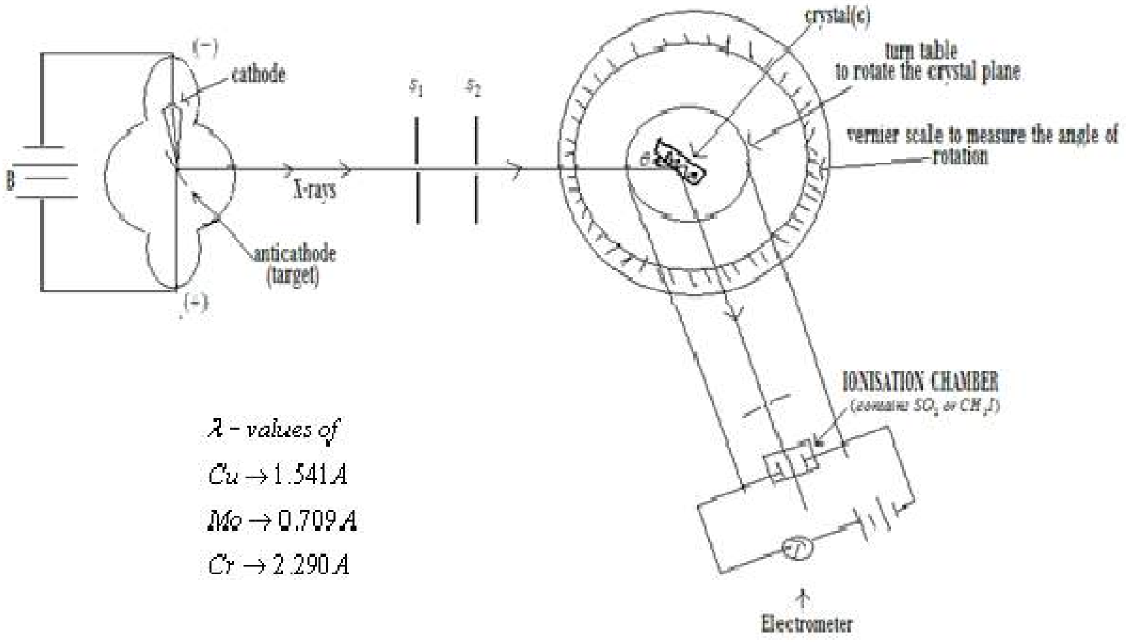
In the Bragg's equation, θ is measured for various order of maximum reflections and the interplanar spacing (d) is calculated by the X-ray diffractometer.

The whole experimental set-up consists of three parts.

(1) X-rays generating component (2) reflection arrangement of X-rays by crystal

(3) Determination of reflected X-ray intensity.

Sketch of Bragg's experimental set-up



Description of the experimental set-up.

The X-rays generated in the X-rays tube are passed through a series of slits to give a sharp and monochromatic beam. The beam is then directed to strike the face of a crystal which is mounted on a graduated rotating table (turn-table). The rays reflected from the crystal are then allowed to pass through a detector, called ionisation chamber, filled with vapours of methyl bromide. The chamber is rotated co-axially with the crystal table. The crystal table and the chamber are so adjusted that when the crystal rotated through any angle, the chamber rotates at twice of that angle so that the reflected rays always enter the chamber. The extent of ionisation produced by the reflected beam is measured by the electrometer.

Details of the experiment.

The value of θ (the incident angle) is gradually increased from 0^o by rotating table. The intensity of the reflected X-rays for various angles is determined. Strong reflections are obtained from those planes which contain larger number of particles (larger particle density) and for those values of θ which satisfy the Bragg's equation. The process is repeated for each plane of the crystal. The intensity of the reflected rays is plotted against θ and the lines are indexed.

Braggs themselves used NaCl crystal and took Pd metal as anticathode (λ = 0.58 A) in the X-rays tube. They examined the maximum intensity of the reflected X-rays from (100), (110) and (111) planes for which the incident X-rays is directed normal to face, edge and corner of the NaCl crystal.

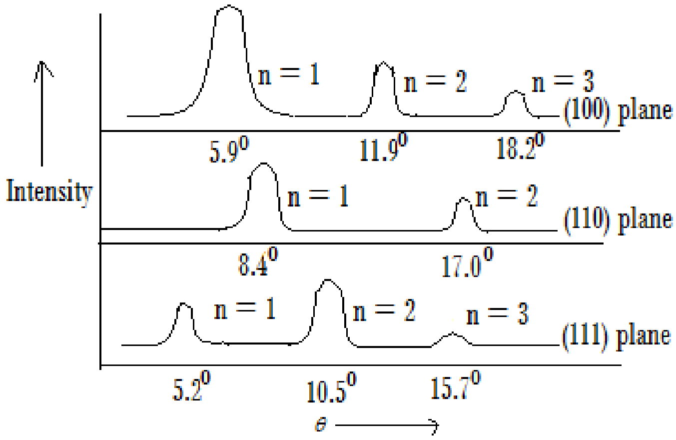
Application of Bragg 's equation to determine the structure of NaCl crystal

To determine the spatial distribution of the particles in a crystal, we need to know the spacing of some chosen crystal planes.

To determine the structure of a crystal, we need to know the pattern of the regularly repeating spatial distribution of the constituents (atoms, molecules or ions). This is possible from the determination of spacing of some suitably chosen lattice planes of the crystal. The spacing are determined by the use of Bragg's equation

$$(2\,d \sin\theta \;=\; n\lambda).$$

Braggs themselves used X-ray diffractometer to determine the crystal structure of NaCl. They used Pd anticathode ($\lambda = 0.58\,A$) in the X-rays tube and examined the maximum intensity reflection of the X-rays from (100), (110) and (111) planes of NaCl crystal. From the graph of reflected X-rays intensity vs. incidence angle (θ) given below,



Intensities of X-rays by different planes

Planes	n = 1	n = 2	n = 3
(100)	100	19.9	4.87
(110)	50.4	6.10	0.71
(111)	9.0	33.1	0.58

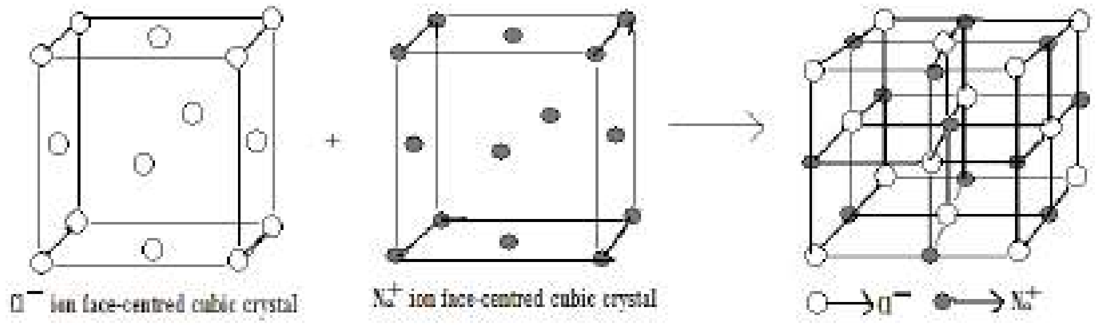
Interplanar distance ratio of NaCl crystal matches with the fcc crystal.

the interplanar distance ratio of these planes can be calculated for n = 1.

$$d_{100} : d_{110} : d_{111} = \frac{\lambda}{\sin 5.9^o} : \frac{\lambda}{\sin 8.4^o} : \frac{\lambda}{\sin 5.2^o} = \frac{1}{0.103} : \frac{1}{0.146} : \frac{1}{0.091} = 1 : 0.705 : 1.14\,.$$

The ratio is also obtained for 2nd order (n = 2) reflections.
The observed ratio of interplanar spacing shows that NaCl crystal is a face-centred cube.
Since in the NaCl crystal, the constituent particles are Na^+ and Cl^- ions, the two face-centred cubic lattices of Na^+ and Cl^- ions are interpenetrating.

Two fcc crystals of Na^+ ion and Cl^- ions interpenetrate to give a fcc NaCl crystal structure.



(111) planes are different from (100) and (110) planes.

Intensity of X-rays reflected by (100) and (110) planes decreases as usual with increase of n, which supports the structure that these planes have both Na^+ and Cl^- .
But for the planes (111), the intensities of n = 1 and n = 3 are low but for n = 2 is high indicating that these set of planes are not identical, either containing Na^+ or Cl^- entirely.
As the Na^+ ions planes are interposed half-way of Cl^- ions planes, (x = d/2), so 1st order and 3rd order intensities are less while 2nd order reflection intensity is high (n = even).
From the structure given, we can calculate the number of NaCl unit per unit cell.

4 units of NaCl are present in the unit cell of the crystal.

Number of Na^+ ions = $8\times\frac{1}{8}+6\times\frac{1}{2}=4$, and number of Cl^- ions = $12\times\frac{1}{4}+1=4$.

Thus, there are 4 NaCl units per unit cell of the crystal. These support the fcc structure.
It is also possible to calculate the interionic distance between Na^+ and Cl^- ions.

Calculation of interionic distance of Na^+ and Cl^- in the crystal.

The spacing of (100) planes is $d_{100}=\frac{n\lambda}{2\sin\theta}=\frac{1\times 0.58A}{2\sin 5.9^o}$ = 2.82A for 1st order refection with Pd anticathode. Thus the interionic distance between Na^+ and Cl^- ions are 2.82 A.
This can again be supported from the density measurement of NaCl substance.

The edge length , $a=\left[\frac{M\times n}{N_A\times\rho}\right]^{1/3}=\left[\frac{58.48\,gm\,mol^{-1}\times 4}{6.023\times 10^{23}\,mol^{-1}\times 2.17\,gm\,cm^{-3}}\right]^{1/3}=5.63\,A$.

So the interionic distance between Na^+ and Cl^- ions = a/2 = 5.63/2 A = 2.815 A.
All these determinations support the face-centre cubic structure of NaCl crystal.

Crystal defects :

So far we have discussed the perfect crystals in which all the constituent particles occupy the right positions as required for the particular geometrical shape.

Imperfection in the crystal alters many physical properties and adds more stability than perfect crystal.

But crystals with perfect lattice are very rare and almost all crystals suffer from imperfections of various kinds. The imperfections in the crystal in many cases determine the electrical properties (such as conductivity), optical properties (colour), transport properties (rate of diffusion) and mechanical properties (compressibility) of the crystal.
At thermal equilibrium, the imperfect crystals suffer more decrease of Gibb's free energy due to increase of disorder in the structure. G = H – TS, S increases and so G decreases.
These crystal defects are of various types.
(A) Line defects : The constituent particles are not arranged in lines as it would be in perfect crystals.
(B) Point defects : It may be of following types.

(1) Impurity defects: If molten NaCl containing little $BaCl_2$ is crystallised, each Ba^{+2} ion displaces 2 Na^+ ions. One site is captured by Ba^{+2} ion and other site remains vacant.

(2) Non-stoichiometric defects: It is of two types.

(a) Metal excess defects: When NaCl is heated in presence of Na-vapour, Na atom deposits on the surface, and Cl^- ion in the crystal moves to the surface and one electron from Na-atom enters into the Cl^- ion position. These acts as F-centre or colour centre.

LiCl crystal becomes pink when heated in presence of Li-vapour and KCl in presence of excess K- vapour becomes violet.

(b) Metal deficiency defects:

(3) Stoichiometric defects:

(a) For non-ionic crystal, it is vacancy defects and interstitial defects.

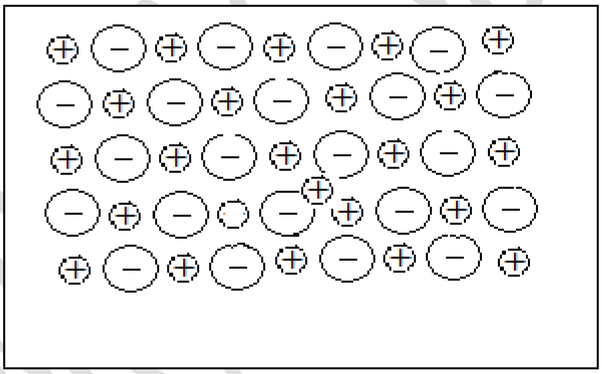
(b) For ionic crystal, it is mainly of two types.

(i) **Frenkel defects:**

In this type of defects, some ions usually cations enter the interstitial positions, leaving a corresponding number of normal lattice sites vacant. The density almost remains same. This defect occurs when one ion (usually cations) is much smaller than the other. As it creates a vacancy defect at its original site and interstitial defect at its new location it is sometimes called dislocation defect.

For example, AgBr and AgCl crystals have such type of defects.

Frankel defect is a misplaced ion site defect.



(ii) Schottky defects: This defect arises when positive and negative ions move to the surface leaving corresponding normal sites vacant. Density of the substance decreases for this type of defect.

This defect normally occurs when anions and cations are of same size.

NaCl, KCl normally contains this type of defect.

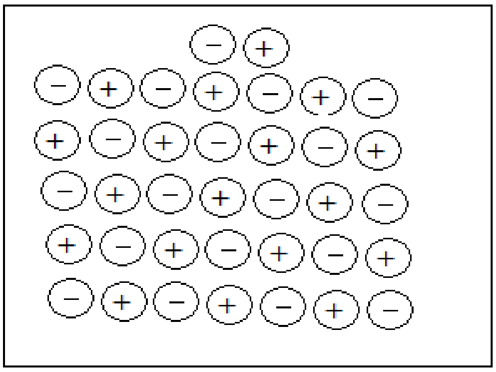
Number of Schottky defects in ionic solids is quite significant. For examples, in NaCl there are approximately 10^6 Schottky pairs per cc at room temperature. In 1 cc, there are about 10^{22} ion pairs

(Molar volume of NaCl = $\frac{58.5}{2.17} = 27\, cc$ thus 1 cc contains $\frac{6\times10^{23}}{27} = 2\times10^{22}$ ion pairs.)

Therefore, one Schottky defect is created per $\frac{2\times10^{22}}{10^6} = 2\times10^{16} \approx 10^{16}$ ions.

Thus , Frenkel defect is a misplaced ion and Schottky defect is a vacant ion site.

Schottky defect is vacant ion site defect.



Tetrahedral and octahedral holes in FCC crystal :

The closed packing of identical spheres occurs in hexagonal closed packed (hcp) and face-centred cubic (fcc) structures. Most of the metal crystals belong to one of these structures. The co-ordination number (equidistance nearest atoms) is 12 in both hcp and fcc. We shall discuss the fcc crystals only.

fcc and hcp are the most closed packed crystal structure.

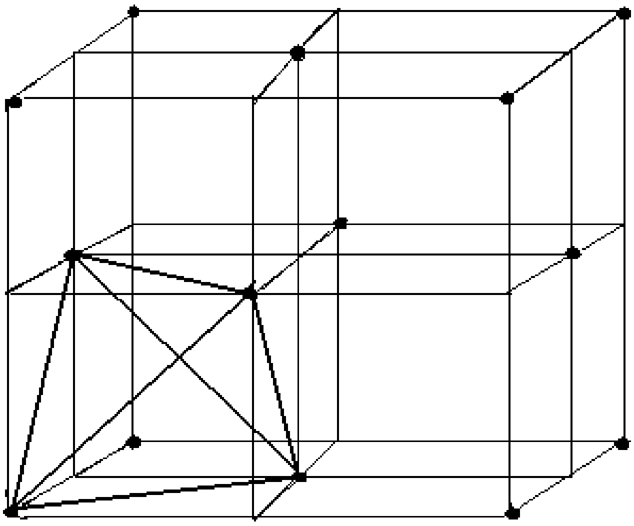
In the above closed packed structures, two types of holes (voids) are generated. While the number of octahedral holes present in a lattice is equal to the number of closed packed particles (4), the number of tetrahedral holes is twice the number ($2 \times 4 = 8$) per unit fcc cell.

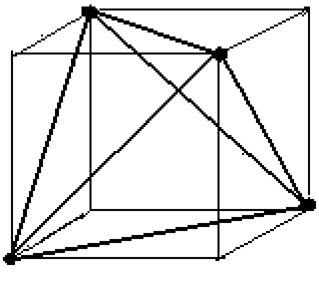
There are two types of holes – tetrahedral and octahedral in fcc crystal.

In ionic solids, the bigger ions (usually anions) form the closed packed structure and smaller ions (commonly cations) occupy the holes. If the latter ion is small enough, it occupies tetrahedral holes and if it is bigger, then it occupies octahedral holes. In a given compound, the fraction of octahedral and tetrahedral holes that are occupied depends upon the chemical formula of the compound.

Locating tetrahedral holes:

Let us consider a fcc unit cell and this unit cell is divided into eight small cubes.





fcc crystal contains eight tetrahedral holes.

Each small cube has atoms at alternate corners. In all, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedral. Thus there is one tetrahedral hole in each small cube and eight tetrahedral holes in total.

But fcc crystal unit cell has 4 atoms and so number of tetrahedral holes is twice the number of atoms in the unit cell.

i.e. number of tetrahedral hole = 2 × number of atoms per unit cell.

It is possible to calculate the diameter of the largest atom to be accommodated in tetrahedral hole in fcc unit cell of edge length ‘a’.

Calculation of the diameter of largest atom to be accommodated in tetrahedral hole

Atoms 1 and 2 in small cube are in contact as shown in the figure, so the atoms are touching along face diagonal of the small cube.

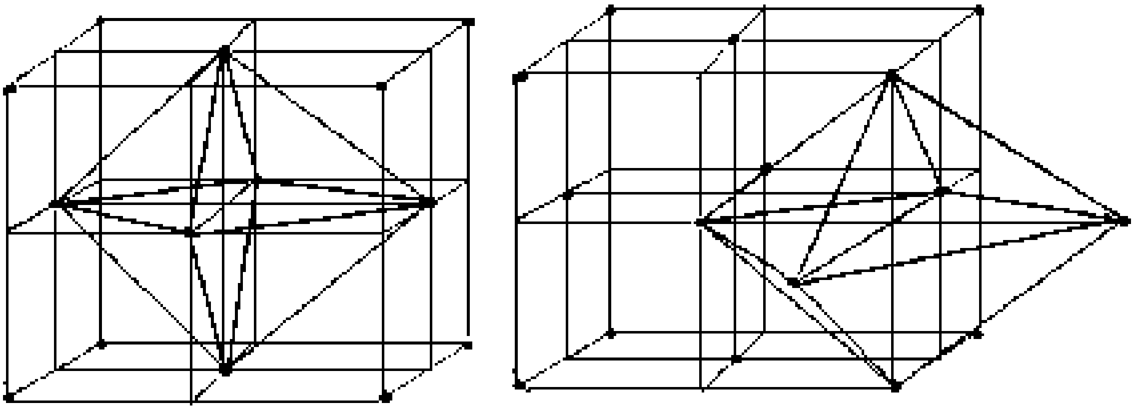
$$2\,r=\sqrt{2}\left(a/2\right) = a/\sqrt{2}\ .$$

Again the centre atom (M) of diameter d is just between the cross diagonal, the length of which is $\sqrt{3}\left(a/2\right)$. Now the two atoms and the centre atom are touching each other along the body diagonal, so $2\,r+d=\sqrt{3}\left(a/2\right)$ or, $d=\sqrt{3}\left(a/2\right)-2r=\sqrt{3}\left(a/2\right)-a/\sqrt{2}$.

Thus, $d=\left(\sqrt{3}-\sqrt{2}\right)a/2$ or, d = 0.16 a.

Locating octahedral holes:

Let us again consider a fcc unit cell, centre of the body of the cube is not occupied but it is surrounded by six atoms on the face centres. If these face centres atoms are joined, an octahedron is generated. Thus, this unit cell has one octahedral hole at the body centre of the cube.



There are four octahedral holes in the fcc crystal.

Besides the body centre, there is one octahedral hole at the centre of each of the 12 edges. It is surrounded by six atoms, four belonging to the same unit cell (2 on the corners and 2 on each face centre) and two belonging to two adjacent unit cells. Since each edge of the cube is shared equally between four adjacent unit cells, so the octahedral hole located on it is also shared by four unit cells. Only ¼ th of each hole belongs to a particular unit cell.

Thus in cube closed packed (CCP) structure,

Octahedral void (hole) at centre of the body of the cube = 1

12 octahedral voids located12 edges and shared between four unit cells = 12 $\times \frac{1}{4} = 3.$

Total number of octahedral (voids) holes = 1 + 3 = 4.

In ccp (fcc) structure, each unit cell has 4 atoms and so number of octahedral holes is equal to this number.

Calculation of the diameter of largest atom to be accommodated in octahedral hole

Calculation of the diameter of largest atom to be accommodated in the octahedral hole of fcc unit cell of edge length ‘a’ is given as,

3 atoms are touching along the face diagonal and so 4 r = $\sqrt{2}$ a.

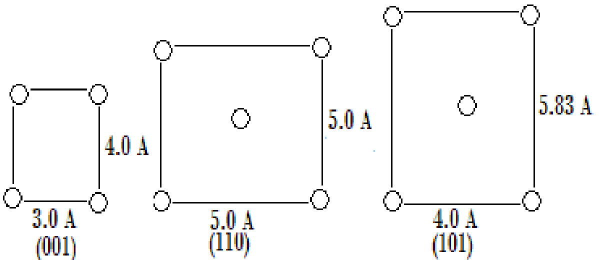
The atom, M to be accommodated at the hole has the diameter, ‘d’ . Then two face centre atoms of the cube and the atom, M in the octahedral hole are touching each other. So,

2 r + d = a, the edge length of the cube or, d = a − 2 r = $a-\sqrt{2}\,a/2 = a\left(1-1/\sqrt{2}\right)$

The largest atom that fits into the hole has diameter, d = $a\left(1-\frac{1}{\sqrt{2}}\right)$ = 0.293 a.

Problem: Copper has a face-centred cubic lattice with a unit cell edge length of 0.361 nm. What is the diameter of the largest atom that could fit into the (i) octahedral and (ii) tetrahedral holes of this lattice without disturbing its structure. [BU'2007, Old pattern]. { Answer : (i) 0.105 nm, (ii) 0.058 nm }

[ISC Entrance' 2003]. **Problems (1):** Shown below the three different crystallographic planes of a unit cell of a hypothetical metal. The circles represent the atom position.

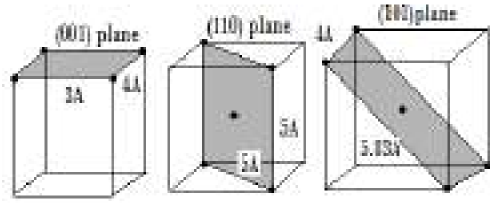


(i) To what crystal system does the unit belong?

(ii) What would be the crystal structure?

(iii) If the density of the metal is 8.9 g cm^{-3} , determine its atomic weight

Ans:



Ans: (i) Orthorhombic.
(ii) Body-centred.
(iii) 160.8.

CU, 2001 3(a) What is meant by a (110) plane? Draw the (110) plane of a simple cubic crystal. (2)

(b) A crystal having simple cubic lattice has the length of its unit cell a_o pm. One of its planes show a first order Bragg reflection at an angle of 60^o. Taking the wave length of the X-ray as a_o pm, find the Miller indices for the plane. (3)

CU, 2002 3(a) What are the Miller indices? (2)

(b) Potassium crystallises with a body-centred cubic lattice and has density of 0.856 g cm^{-1} . Calculate the length of the unit cell and the distance between (110) planes. (3)

CU, 2003 3(a) Is it possible to obtain Bragg reflection from (100) plane of a simple cubic crystals with edge length 1.5 A by using X-rays with wavelength 3.5 A? (2)

(b) The density of Lithium metal is 0.53 $g.cm^{-1}$ and the separation of the 100 planes of the metal is 350 pm. Determine whether the lattice is f.c.c. or b.c.c. [M of Li = 6.94 $g.mol^{-1}$]. (3)

CU, 2004 3(a) With the help of a diagram show that for a cubic lattice the spacing between the adjacent (hkl) planes is $d=\frac{a}{\sqrt{h^2+k^2+l^2}}$, 'a' is the edge length. (3)

CU, 2005 (2)(b) The smallest observed Bragg diffraction angle of the reflection from (111) planes of a potassium crystal is θ=6.613 when X-radiation of wavelength λ = 70.926 pm is used. Given that potassium exists as body-centred cubic lattice, determine the length of the unit cell and density of the crystal (At. wt. of K = 39). (2+2)

Civil Service Exam. 2000,

3(a) Calculate the closed distance between the atoms placed in a face-centred unit cell.

(c) For identical experimental conditions the first order Bragg reflection from a plane of a cubic crystal comes up at 5.9° and 5.85° respectively at 20°C and 50°C. Calculate thr coefficient of cubic expansion of the solid. (3)

4(c) A unit of NaCl crystal contains 14 chloride and 13 sodium ions and yet it contains 'four' molecules of NaCl . Explain.

CSE, 2001

1(d) Calculate the wave length of X-rays if the reflected angle for NaCl with density 2.163 g/cc is 5.9°.

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