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Module-05 Lecture-02 Kinetic Theory of Gases - Part 02

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After doing the angular integration (which comes out to be 1/3), the total pressure due to atoms of all speeds is given by $PV = \frac{1}{3} m \int_0^\infty v^2 dN$ The average of the square of the atomic speeds $\langle v^2 \rangle$ is defined to be $\langle v^2 \rangle = \frac{1}{N} \int_0^\infty v^2 dN$ so that we have $PV = \frac{Nm}{3} \langle v^2 \rangle$ This is a famous equation of the kinetic theory of perfect/ideal gases

So, after doing the angular integration which comes out to be one third, the total pressure due to atoms of all speed ranges from 0 to infinity is given by P times V is one third which is due to the angular integration 0 to 2 Pi d Phi 0 to Pi by 2 cos square theta sine theta d theta divided by 2 Pi this will comes about 2, this will come about to be one third m 0 to infinity square into dA.

The average of the square of atomic speed which is known as the root mean square speed is defined to be v square average is 1 by N 0 to infinity v square times dN. This is known as the root mean square velocity which is defined as the average of the square of the velocity. So, that we have PV = n Capital N which is the total number of atoms or molecules times mass m divided by 3 into root mean square velocity.

This is the famous equation of the kinetic theory of perfect or ideal gases. Now let me write down this equation in other form also.

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Now, mN =M is the mass of the gas and

$$\frac{mN}{V} = \frac{M}{V} = \rho$$

where ρ is the density of gas. Then the pressure of the gas becomes

$$P = \frac{1}{3}\rho\langle v^2 \rangle = \frac{2}{3}E,$$

.....(1

where $E = \frac{1}{2} \langle v^2 \rangle$ is the kinetic energy per unit volume.

Thus the pressure of a perfect gas is numerically two-third of the kinetic energy per unit volume. This equation is called basic equation of the kinetic theory of gasses.

Now a small m into Capital M = small n m into capital N = Capital M which is the mass of the gas? So, in terms of this so which is nothing but the M by V which will give you the Rho. Where Rho is the density of gas then the above equation can be rewritten in terms of P = one third Rho v square average. So, where Rho is the density of the gas or = two third E where E the kinetic energy per unit volume which is half times root mean square velocity.

So, this is another way to write down the equation in the, of the kinetic theory of gases. First way is to write down in terms of PV, second way you can write down in terms of P in terms of the density of the gas. Thus the pressure of a perfect gas is numerically two third of the kinetic energy per unit volume. This equation is called the basic equation of the kinetic theory of gases.

In deriving equation 1 we have made no assumptions about the nature of molecular impact against the wall. We have not made any assumptions what is the nature of molecular impact against the wall.

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In deriving equation (1) we have made no assumption about the nature of molecular impact against the wall.

From equation(1) the mean square velocity of the molecules of a gas is

$$\langle v^2 \rangle = \overline{v^2} = \frac{3P}{\rho}$$
(2

Hence the root mean square (R.M.S.) velocity is given by

$$C = \sqrt{v^2} = \sqrt{\frac{3P}{\rho}} \qquad \dots (3)$$

Knowing the pressure and density of a gas experimentally, v^2 and hence C can be calculated.

Now let me see what is the mean square velocity of the molecules of a gas, mean square velocity from that equation 1 we can see it is 3 P by Rho where P is the pressure and Rho is the density of the gas. Hence the root mean square velocity is given by, is square root of 3 P by Rho that means if the density of the gas is large in that case root mean square velocity will be small. If the density of the gas is very low root mean square velocity will be very large.

Knowing the pressure and the density of a gas experimentally people have calculated root mean square velocity and hence C can be calculated.

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Kinetic Interpretation of Temperature

Let us consider a gram molecule of a gas, which occupies a volume V. From equation (1), we get

$$PV = \frac{1}{3}M\langle v^2 \rangle, \qquad \dots (4)$$

where M is the molecular weight.

In the kinetic consideration of a perfect gas, we use the gas equation.

where R is the gas constant and T is the absolute temperature. Comparing equation (4) and equation (5) we get

$$\langle v^2 \rangle = \frac{3RT}{M} \qquad \dots \dots (6)$$

Kinetic interpretation of temperature, till now I did not talk about what is the concept of temperature? How the concept of temperature has come? So, let me start it, let us consider a gram molecule of a gas which occupies a volume V from equation 1 we can get PV = one third M times average values of v square which is nothing but the root mean square velocity.

In the kinetic consideration of a perfect gas we use the experimental equation of state which is PV = RT in that case where R is the gas constant and T is the absolute temperature. If you will compare the equation 4 and 5 what you will see average values of v square which is the root mean square velocity which comes out to be 3 RT by M. Where R is the universal gas constant M is the mass of the gas.

That means if R and M are constant and which is indeed true then average values of v square is proportional to t where t is nothing but the temperature.

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Thus $\langle v^2 \rangle$ is proportional to the absolute temperature. This is the kinetic interpretation of temperature.

According to the kinetic theory, all the molecules should have zero velocity at absolute zero of temperature.

However, this result is not quite justified as ceases to behaves as a perfect gas before reaching the absolute zero of temperature.

Again if we write $M = mN_A$ where N_A is the Avogadro number, then equation (6) can be written as

$$\frac{1}{2}N_{A}m\langle v^{2}\rangle = \frac{3}{2}RT \qquad \dots (7)$$

Or other way around v square is proportional to the absolute temperature. This is the kinetic interpretation of temperature. That means till now we did not know what is temperature? Now we come to know temperature is nothing but it is a measure of the average values of the kinetic energy. Average values of the kinetic energy means how you have got v square by 3 this is because of the isotropycity of momentum in the momentum space.

Where average values of Vx square = average values of Vy square = average values of Vz square. That means in other way around temperature is nothing but whenever there will be equilibration in the momentum space that situation is known as he is coined as the temperature ok. So, according to the kinetic theory all the molecules should have 0 velocities at the absolute 0 of the temperature.

However this result is not justified as C just to behaves as an ideal gas before reaching the absolute 0 of temperature because whenever you approaches the absolute 0 temperature that times the concept of perfect gas ceases to exist. At various small temperatures there is no gas which can be called as an ideal gas, only ideal gas the realization of ideal gas holds good at very large temperature and very low density.

So, that is the reason you cannot simply extrapolate that as temperature tends to 0 the velocity tends to 0. So, simply you cannot extrapolate it. Again if you write capital M = small m into NA where NA is the Avogadro number then the above equation 6 can be written as half NA times m into have average values of v square = 3 by 2 RT.

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or
$$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} kT$$
(8)

where $R = N_A k$ and k is the Boltzmann constant.

Hence the mean kinetic energy of translation of one molecule is

$$\frac{3}{2}kT$$

Thus the mean kinetic energy of translation of the molecules can be regarded as a measure of temperature.

Where R by NA = K where K is the Boltzmann constant so finally we got the equation half m average values of v is v square = 3 by 2 KT. Thus the mean kinetic energy of translation of molecules can be regarded as a measure of temperature. However in that case the average energy

per atom is wholly kinetic energy of translation. Now the concept of monatomic gas will play the

major role.

In case of monatomic gas the kinetic energy is purely translation in character. Whereas if you

will go to the diatomic gases although the diatomic atoms not interacting with each other but it

can rotate, it can vibrate with respect to the axis passing through its equilibrium position. So, that

is the reason the average values of kinetic energy whether it will be the 3 by 2 KT or other values

it depends on whether it is a monatomic gas or whether it is a diatomic gas, whether it is it

triotomic gas.

In our cases since we have started the kinetic theory for the monatomic gas, monatomic gas have

only translational kinetic energy. It cannot have rotational or vibrational kinetic energy because it

does not have those degrees of freedom. So, this is the only kinetic energy that a hard spherical

atom on influenced by its neighbor or field can have. Therefore we have limited ourselves to

monatomic gas only.

Diatomic and polyatomic molecules can only can also rotate and vibrate and may therefore be

expected to have energies of rotation and vibration. Even though there are no forces between the

interacting molecules. But till now we will not talk about the kinetic theory of gases for the

diatomic or polyatomic gases.

In the next part of my lectures we will confine ourselves only to the monatomic ideal gases.

Whenever we used to claim that we are giving a new theory, new microscopic theory. So, we

have to define we have to calculate some quantities and let and tally with the experimental result.

So, let us calculate the internal energy of a gas of atoms using the kinetic theory of gases.

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Internal Energy

In kinetic theory, it is assumed that atoms behave as noninteracting particles, so the potential energy of their interaction may be neglected. The only form of energy these particles may possess is translational kinetic energy. They may not possess, for example, rotational or vibrational energies. Therefore, the internal energy of the ideal monatomic gas is the sum of the kinetic energies of all its atoms:

$$U = \sum_{j} \frac{1}{2} m v_{j}^{2} = N(\frac{1}{2} m < v^{2} >)$$

Using the above equation to replace the kinetic energy, we obtain a calculated expression for the internal energy of a monatomic ideal gas.

$$U = \frac{3}{2} nR T$$

→The internal energy of the ideal monatomic gas, calculated from the kinetic theory of gases, is proportional to the thermodynamic temperature only. This agrees with the experimental results.

In kinetic theory it is assumed that atoms behave as non interacting particles. As we have told you that there is no interactions among atoms only interaction are occurring between the atom between the collision of atoms with the walls of the gas. So, the potential energy of their interaction and may be neglected. The only form of energy these particles may possess is the translational kinetic energy.

They may not possess for example rotational or vibrational degrees of freedom. However in case of monatomic gas there are no rotational and vibrational degrees of freedom. So, there is no kinetic energy which are associated with the rotational vibration okay. So, therefore the internal energy of the ideal monatomic gas is the sum of kinetic energies of all its atoms that means U is summed over half myj square who are J runs from all atoms in the gas okay.

So, I can take out so which is nothing but the N times half m average values of v square. So, using the above equation to replace the kinetic energy we obtained a calculated expression for the internal energy of a monatomic ideal gas which is U = 3 by 2 nR T where n is the number of moles R is the universal gas constant T is the temperature. So, the internal energy of ideal monatomic gas calculated from the kinetic theory of gases is proportional to the thermodynamic temperature only.

And this agrees with the experimental result, however we have already seen from the thermodynamics that internal energy depends only on temperature. But we do not know how to get it. So, this is the beautiful aspect of the kinetic theory through which we have started from the microscopic point of view which deals with the constituent of the system and finally we have lamp landed up with a beautiful expression which is which dependent which shows that internal energy does depend only on temperature only.

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→In the kinetic theory of gases, the concept of temperature is primarily a foreign element, since, in fact the individual atoms are characterized by their speed alone. But, it is suggestive that we should define the ideal-gas temperature in terms of the mean kinetic energy.

→ What should the important point to mention here?

These above results have been derived from the laws of physics and statistics, rather than being formulated from experimental data.

In the kinetic theory of gases the concept of temperature is primarily a foreign element since in fact the individual atoms are characterized by the speed only. But it is suggestive that we should define the ideal gas temperature in terms of the mean kinetic energy. So, last but the least I want to mention what is the beauty of the kinetic theory of gases. What are the most important point which should be mentioned in this lecture?

Those above results for whatever we have derived, has been derived from the laws of physics and statistics rather than being formulated from experimental data which usually which has been done in the theory of thermodynamics. But in case of kinetic theory of gases we have derived it from the laws of physics and statistics. And from the first principle of calculation and it has come automatically that the expression of the internal energy.

So, next we want to convince ourselves that whatever we have derived it whether it can reproduce the known laws which is known to us since 4 to 500 years ago. So, let us derive those laws from the kinetic theory of gases okay.

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Deduction of gas laws

Some fundamental law of a ideal/perfect gas can be deducted from the basic equation (s) which we have just derived.

(a) Boyles' and Charles' law

We consider a gram-molecule of a gas at absolute temperature T occupying volume V. We have

$$PV = \frac{1}{3}mN\langle v^2 \rangle$$

According to the kinetic theory, the mean square velocity of the gas is proportional to its absolute temperature i.e.

 $\langle v^2 \rangle = \alpha T$, where α is a constant,

hen above equation give:

$$PV = \frac{1}{2}mN\alpha T$$

Some fundamental law of ideal of phosphate gas can be deducted from the basic equation which we have already derived. First Boyles' and Charles law we consider a gram mole of gas at absolute temperature T occupying volume V, so, that we have PV = one third mN v square average. According to the kinetic theory the mean square velocity of the gas is proportional to the absolute temperature.

So, v square of arras proportional to T where = alpha times T where alpha is a constant. So, the above equation we see that PV is one third mN into alpha into T.

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Hence at a given temperatures P V = constant Boyles' Law For a fixed amount of an ideal gas kept at a fixed temperature, P [pressure] and V [volume] are inversely proportional (while one increases, the other decreases). Again from the equation: $P V = \frac{1}{3} m N \alpha T$ we get $V = \frac{m n \alpha}{3 P} T$ $V \infty T, \text{ when P is held constant.}$ At constant pressure, the volume of a given mass of an ideal gas increases or decreases by the same factor as its temperature on the absolute temperature scale (i.e. the gas expands as the temperature increases)

So, at a given temperature PV = constant which is nothing but the Boyle's law. As we know what does it mean by Boyle's law? For a fixed amount of ideal gas kept at fixed temperature P pressure and volume are inversely proportional to each other. While one increases other decreases this is Boyle's law. The Boyle's law is based on the empirical observation since 100 and 100 years.

But from the kinetic theory of gases we have got this law automatically we did not take any assumptions we did not get, we did not analyze any experimental result it has come automatically from the kinetic theory of gases that is the beauty of any microscopic theory. Again from the same equation if you rewrite in other way V is V is proportional to T when P is held constant which is nothing but the Charles law.

So, what is Charles law? At constant pressure the volume of a given mass of an ideal gas increases or decreases by the same factor as its temperature on the absolute temperature scale. So, that means the gas expands at temperature increases as gas shrinks as the temperature decreases. So, this is Charts law and again the emphasis is given to the kinetic theory of gases the Charles law which is based on the empirical observation.

Since 100 and 100 years but from the kinetic theory of gases these Charles law has come automatically that is the beauty of the kinetic theory of gases. We have already told how Charles

law, Boyle's law could come out automatically from the kinetic theory of gases. Let me tell how Avogadro laws could come automatically from the kinetic theory of gases. Let me see how it can it can be derived automatically.

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(b) Avogadro's law

Let two ideal gases 1 and 2 have the equal volume at the same temperature and pressure. When the two gases are at the same pressure P, then we have from the kinetic theory

$$PV = \frac{1}{3} m_1 N_1 \langle v_1^2 \rangle = \frac{1}{3} m_2 N_2 \langle v_2^2 \rangle$$

When the two gases are at the same temperature, the average kinetic energy of molecule of both the gases are same, i.e.,

$$\frac{1}{2}m_1\langle v_1^2\rangle - \frac{1}{2}m_2\langle v_2^2\rangle$$

Combining the above two equations, we get

$$N_{\perp} = N_{\perp}$$

Thus equal volumes of all gases under the same conditions of temperature and pressure have same number of molecules.

→ Avogadro's Law

Let us see let the two ideal gases gas 1 and gas 2 have the equal volume at the same temperature and pressure. When the two gases are at the same pressure then we have from the kinetic theory that this would have the same kinetic energy. Because we know that since P pressure volume and other pressure and volume remains the same. So, that means the average kinetic energy of the gas1 should match with the average kinetic energy of the gas2.

So, that means PV = one third m1 N1 v1 square average = one third m2 N2 into v square average. When the two gases are at the same temperature, let us say they are temperature is also same so that means their average kinetic energy of the gas1 and gas2 should be the same because temperature is a measure of the average kinetic energy. Since we are saying temperature remains the same if the temperature held constant.

Then the average kinetic energy of the gases 1 = should be the same as the average kinetic energy of the gas2. So, that means the average kinetic energy of molecule of both the gases are the same so that means half m 1 v1 square average = half m2 v2 square average. If you will combine these two equations we will get N1 = N2 that means number of atoms or molecule in

gas1 should be = the number of atoms or molecule in the gas2 which is nothing but the famous Avogadro's laws okay.

The beauty again it should be emphasized beauty of this derivation is that it is not based on the experimental data since years and years. It has come automatically from a microscopic theory in our case it is the kinetic theory of gases. Thus equal volumes of all gases under the same conditions of temperature and pressure have the same number of molecules which is the celebrated Avogadro's law.

Now next go to the laws of partial pressure Dalton's law of partial pressure. So, as we have already told you in the first transparency, as we have already told you in the very first transparency that gases are infinitely miscible that means gases mix in any proportion such has in air, a mixture of gases, so, when you will mix the two gases what will be the total pressure.

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(c) Dalton's law of Partial Pressure

Let there be a mixture of number of gases of densities ρ_1 , ρ_2 , ... and of mean square velocities, $\langle v_1^2 \rangle$, $\langle v_2^2 \rangle$,... ... in the same volume V, then the total pressure exerted by the mixture is given by

$$P = \frac{1}{3}\rho_1 \langle v_1^2 \rangle + \frac{1}{3}\rho_2 \langle v_2^2 \rangle + \dots$$

$$= P + P + \dots$$

where $P_{\rm L}/P_{\rm L}$ are the partial pressures exerted by different components of the mixture occupying the volume V. Thus the pressure exerted by the mixture is equal to the sum of the pressures exerted separately by its components.

→ Dalton's Law of Partial pressure.

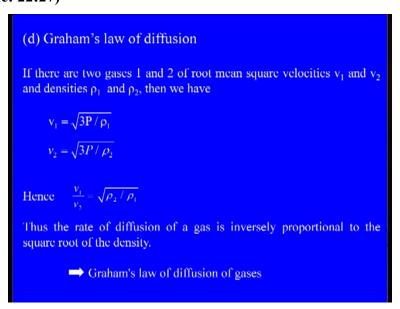
So, so let me start let there be a mixture of number of gases of densities Rho1, Rho2 and of mean square velocity is v1 square, v2 square in the same volume P that means in a given volume you have taken two gases and you mix them. Then the total pressure exerted where the mixture is given by P pressure since it is a scalar norm quantity. So, the pressure could be added together so, pressure due to the gas.

One will be half one third Rho1 v1 square average where Rho 1 is the density of the gas1, v1 square average is the mean square velocity of the gas1 +one third Rho2 v2 square this is due to the gas2 where Rho 2 is the density of gas 2 and v2 square is their average velocity of the gas2 which is nothing but the P1 + P2 which is nothing but the pressure exerted by the gas1 plus pressure exerted by the gas2 and the pressure exerted by the other gases.

So, where P1, P2 are the partial pressure exerted by the different components of the mixture occupying the same volume V. So, thus the pressure exerted by the mixture as a whole is = the sum of the pressures exerted separately by the individual components. So, that means if there are n component gases are there so that means the pressure of the n component gas should = the sum of the pressure by the individual components that means P should be summed over PA.

Where I ranges from 1 to n where n is the number of components. So, this is nothing but the famous Dalton's law of partial pressure. Again the emphasis goes back to the kinetic theory it has come these Dalton's law of pressure has come automatically from the kinetic theory of gases without any experimental data.

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Graham's law of diffusion this is a very famous law of diffusion what is it? So, now let us take two gases gas1 and gas2 and obviously since there are two different gases they are root mean square velocities will be different. Let us take the root mean square velocity of the gas1 and gas2

are v1 and v2 respectively and their densities are also Rho 1 and Rho 2 respective. Then we

know from this relation of this relation of group mean square velocity which is nothing but the

square root of 3 P by Rho.

We can write down the root mean square velocity for the two gases separately. First one is v1 =

root over 3P by Rho 1 where Rho 1 is the density of the gas1 and velocity would mean square

velocity v2 for the gas 2 is 3P by Rho 2 where Rho 2 is the density of the gas 2. Now if I will take

this ratio what I will get v1 by v2 is = square root of Rho 2 by Rho 1. So, that means root mean

square velocity is proportional to proportional to 1 by square root or it is inversely proportional

to the square root over their density.

That means if the density of the gases are large their root mean square velocity will be very

small. If the densities are very small then the root mean square velocity will be very large. So,

using the density dependent or root mean square velocity the gas diffuse accordingly thus the rate

of diffusion of a gas universally proportional to the root square root of the density this is famous

Grahams law of diffusion of gases.

Using this Graham's law of diffusion of gases we can see in our nature why one gas are diffuses

more rapidly compared to the other gas because of their origin of the root mean square velocity

depends on their density inversely.

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Computation of various constants

Avogadro Number N_∧

If m be the mass of a molecule, then the molecular weight is

$$M = mN_A$$

or $N_A = \frac{N}{m}$

For H_2 gas, M = 2 and $m = 3.32 \times 10^{-24}$ gm, then

$$N_A = \frac{2}{3.32 \times 10^{-24}} = 6.024 \times 10^{23} \text{ mol}^{-3}$$

We can calculate some various constant using the kinetic theory of gases. However we know the values of constant earlier because of some experimental data. But the values of some constant will come beautifully from the kinetic theory of gases. Those are very famous constants, first is Avogadro number. The number of atoms or molecules in one gram mole of gas, so, if m is the mass of a molecule then the molecular weight is capital M = small m into number of particles which could be they Avogadro number.

So, Avogadro number NA = molecular weight by the mass of a molecule. For a hydrogen gas M = 2 molecular weight and small m mass of a hydrogen molecule is 3.32 into 10 to the -24 gram. If we will put there then num Avogadro number will comes out to be 2 by 3.32 into 10 to the -24 = 6.024 into 10 to the 23 number of particles per mole. So, this is the Avogadro number which comes out to automatically from this.

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2. Universal Gas Constant, R
For one gram- mole gas, we have the relation PV = RT \quad \text{or} \quad R = \frac{PV}{T}
At normal pressure and temperature (N.T.P.)
P = 76 \text{cmHg} = 76 \times 13.6 \times 78 \text{ ldyne/cm}^2
= 1.013261 \times 10^6 \text{ dyne/cm}^2 = 1.013961 \times 10^5 \text{ N/m}^2
V = 22.4 \times 10^3 \text{ cm}^3 \qquad T = 273 \text{ K}
R = \frac{\left(1.013961 \times 10^6\right) \times \left(22.4 \times 10^3\right)}{273} = 8.31 \times 10^6 \text{crg/molk} = 8.31 \text{J/molk}
= \frac{8.31 \times 10^7}{4.18 \times 10^7} \text{Cal/molk}
= 1.99 \text{Cal/molk}.
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Second universal gas constant which is a very famous constant which is known as the universal gas constant R for one gram mol gas we have the relation PV = RT because N has become = 1 so R = PV by T. Let us calculate at normal pressure and temperature NTP we know at normal pressure P is 76 centimeter of mercury, so, which is nothing but in terms of calculating the CGS units 76 into 13.6 into 78 1 Dynes per centimeter square.

Which is = 1.02 into 10 to the power 15 Newton per meter square, volume as we know in the normal pressure and temperature one mole gas occupy 22.4 liter volume, so, V is 22.4 into 10 to the 3 cc. Temperature is 220 mm 273 degree Kelvin. So, if you substitute all these values in the equation R = PV by T, we will R will comes out to be 8.31 Joule per mole Kelvin. In terms of other in terms of calorie it will comes out about 1.9 and calorie per mole degree Kelvin.

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3. Boltzmann Constant, k By definition, Boltzmann constant (k) is given by $k = \frac{R}{N_A} = \frac{8.31 \times 10^7}{6.024 \times 10^{23}}$ $= 1.38 \times 10^{-16} \text{erg} / \text{K}$ $= 1.38 \times 10^{-23} \text{J/K}$

First, last but the least Boltzmann's constant which is a very fundamental in the sense these Boltzmann constant is the first constant which connects to the microscopic world through the famous relation of entropy = entropy is proportional to the logarithmic of the number of accessible microstates and proportionality constant is Boltzmann's constant.

This relation is fundamental in the sense this is the first relation which connects the macroscopic world means thermodynamics to the microscopic world the number of possible microstates through the Boltzmann's constant. You can calculate Boltzmann's constant through this beautiful relation which we have already come across in the kinetic theory of gases earlier. This here let me show you the earlier transparency.

This R by A = K where K is the Boltzmann constant, so k = R by NA, NA is the number Avogadro's number, R if you will substitute the values of R and NA then k will comes out to be 1. 38 into 10 to the power 16 R per degree Kelvin, in terms of Joule it will comes out to be 1.38 into 10 to the -23 Joule per Kelvin.