

Introduction to Atmosphere and Space Science
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Lecture – 18
Thermodynamics – Dry Air

Hello, dear students. So, now, we will continue discussions on the gas constant; the universal gas constant and other aspects of Thermodynamics. So, we have seen in the last class that, we define what is called as the specific gas constant of the particular type of gas; of a certain type of gas for 1 kg of mass let say.

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Gas laws


- Here, R is a constant called the gas constant for 1 kg of a gas.
- The value of R depends on the particular gas.
- We can also write the gas equation using the density as $p = \rho RT$
- For a unit mass (1 kg) of gas we can write the equation as $p\alpha = RT$
- Where α is the specific volume of the gas (volume occupied by 1 kg of the gas at pressure p and temperature T)

So, this constant is called as the gas constant or this is also called as the specific gas constant. So, this is specific gas constant for a given type of gas for 1 kg of mass right.

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Gas laws

- We define a gram-molecular weight (mol) of any substance as the molecular weight M of the substance expressed in grams.
- Example: 1 mol of water is 18.015 g of water.
- The number of moles in mass m (in grams) of a substance is given as
$$n = \frac{m}{M}$$
- A kilomole of one gas must contain the same number of molecules as a kilomole of any other gas.
- The number of molecules in a kilomole of any material is a constant known as Avagadro number i.e., $N_{A^*} = 6.022 \times 10^{26}$ per kilomole

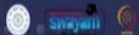


Then, we define the number of moles and we realized the number of molecules in a kilo mole of any material is a constant known as the Avagadro's constant or Avagadro's number. So, any gas of 1 kilo mol; that means, any gas weight divided by the molecular weight will have the same number of molecules and the Avagadro's hypothesis says that gases containing the same number of molecules occupy the same volume at the same temperature and the pressure right.

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Avagadro's hypothesis

- According to the Avagadro's hypothesis, gases containing the same number of molecules occupy same volume at the same temperature and pressure.
- So, a kilomole of any gas the value of gas constant is the same and is referred to as Universal gas constant R^*
- The value of R^* is 8314.2 J/deg/kmol



So, this is the most important thing. So, you keep the temperature and pressure constant will occupy the same volume right. Now, you define another gas constant or so; that means, that a kilo mole of any gas, the value of gas constant will be the same. So, here what you are doing is, you have defined R star is called as the universal gas constant. Universal gas constant is 8314.2 Joule per degree per kilo mole per kilo mole.

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Gas constant

- We know that for a specific gas $R^* = MR$
- We can thus write the ideal gas equation for n kilomoles of any gas as $pV = nR^*T$
- The gas constant for one molecule of any gas is also a universal constant known as Boltzmann constant $k = \frac{R^*}{N_A}$

Handwritten notes:
 R: for 1kg of a gas
 R*: 1 kilomole of any gas
 $pV = nR^*T$
 $k = \frac{R^*}{N_A}$

So, we know that for a specific gas, the gas constant can be defined again from R star is equals to M times R right. So, R is your specific gas constant right. So, basically the idea was you have defined R for 1 kg of a gas, a particular type of gas and you have defined R star which is the same for any 1 kilo mole of any gas. So, you have you take the molecular weight, then you can get back the R star as R times capital M.

So, we can thus write, you can use this equation into the earlier gas equation which was P alpha is equals to R T you can use in terms, instead of R you can use R star by M times T. So, which you can write as so, the number of moles, p V is equals to n R star T. So, the gas constant for 1 molecule of gas. Now, gas constant for 1 kilo mole of any gas is the universal gas constant. Gas constant for 1 kg of a specific gas is the specific gas constant.

Now, gas constant for 1 molecule of any gas. So, you take the universal gas constant, you divide the Avagadro's number of 1 kilo mole the number of molecules of 1 kilo mole, because this R star is eventually R star is has is 1 kilo mole of a gas. So, it divides by the number of molecules that this 1 kilo mole will have which is a constant again. So, the

universal gas constant divided by the number of molecules in 1 kilo mole is again a constant which is called as the Boltzmann's constant. So, we make use of all these constants at several instances right.

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Gas law – dry air

- For any gas containing n molecules per unit volume, the ideal gas law can be written as $p = nkT$ $\frac{R^*}{V_d} mF$
- We consider dry air as the mixture of gases in air including water vapor.
- If the pressure and specific volume of dry air are p_d & $\alpha_d \Rightarrow p_d \alpha_d = R_d T$ dry air
- Where R_d is the specific gas constant for 1 kg of dry air.

Let say for example, dry air. So, what is dry air? Dry air is the mixture of gases that, we see in our atmosphere. Generally, we do not; we do not talk about moisture, then we are talking about dry air. So, for any gas containing molecules per unit volume; n number of molecules per unit volume. So, n is eventually a number, number of molecules per unit volume. So, it has the dimensions of 1 by volume right.

It does not have any dimensions of the mass right. It has the dimensions of 1 by volume or mass by volume is the density right. So, you can get rid of the density and replace it with number of molecules per unit volume, we can write that equation of state as p is equals to $n k T$ right. So, this volume term is now is in this and the Boltzmann's constant has the information of R star by N_A into n into T right.

So, we consider dry air to be the mixture of gases in atmosphere including water vapor ok. So, dry air is the air that we see around ourselves right. Now, let say if the pressure and specific volume of dry air are. So, pressure is p_d and the specific volume occupied by 1 kg of air is α_d . Then, we write the equation of state as $p_d \alpha_d$ is equals to $R_d T$. See here, the suffix d indicates it is for dry air. So, it is not for a single species gas it's for a mixture of gases.

Generally, we know that mixture of gases is oxygen, nitrogen, carbon dioxide, argon right. So, this is the combination that we know very well in the lower altitudes in up to let say 10 kilometers or 5 kilometers right. So, this mixture of gases is referred including water vapor; including water vapor this mixture of gases is called as the dry air fine. So, if you take dry air, if you know what is the pressure that it dry air exerts p_d . What is the volume that 1 kg of dry air will occupy; α_d , if you know what temperature is at which you have made the measurements that is capital T.

You can write the gas equation as $p_d \alpha_d = R_d T$, where R_d is the specific gas constant for 1 kg of dry air right, 1 kg of dry air right. Now, you can form 1 kg of dry air out of different proportions of O₂, N₂, CO₂, argon and H₂O right, but in the atmosphere, we know what proportions are these gases existing right. So, we can calculate 1 kg of dry air can be made up out of these gases at a particular proportion right.

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Apparent molecular weight

- We can now define the apparent molecular weight of dry air as the total mass of constituent gases in dry air divided by the total number of moles of constituent gases.

$$M_d = \frac{\sum m_i}{\sum \frac{m_i}{M_i}}$$

Handwritten notes: CO_2, N_2, O, H_2O

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

$$M_d = \frac{m}{\sum n_i} = \frac{m}{\sum \frac{m_i}{M_i}}$$

Handwritten note: $R^ = MR$*

So, now here we define what is called as the apparent molecular weight. Previously the molecular weight the idea of molecular weight was with the assumption that, whenever you talk about a gas system it is a single species gas, but here we have a mixture of gases. So, we can now define the apparent molecular weight of dry air as the total mass of constituent gases in dry air divided by the total number of moles of constituent gases, understand.

So, in the number of moles; the idea of number of moles is the weight let say divided by molecular weight. So, generally, we write it as small m; weight divided by molecular weight.

So, here we define the apparent molecular weight; apparent molecular weight of a mixture of gases as the total mass of constituent gases in dry air divided by the total number of moles of constituent gases because unequal number of moles will be present in the total 1 kg of air that you take right.

So, simply with this idea so, here n is what m by capital M right. So, now, here capital M the apparent molecular weight. So, this is if it is a single species gas, you will simply write capital M , if it is a multi species gas or if it is a mixture of gases, the apparent molecular weight, let say we call it as M_d is nothing, but m by n . Now, n is the number of moles. So, the total number of moles are to be calculated out of number of moles of each gas.

So, sum over m_i , what it means is sum over the mass of individual gases; oxygen, nitrogen and so on, divided; so it has to be sum of n_i ; sum of n_i is now, number of moles is again weight by molecular weight right. So, mass of i th species divided by the molecular weight of i th species right. So, here you make this; you substitute this into this. So, eventually you are getting this.

So, mean molecular weight or the apparent molecular weight of dry air is defined as the total mass of the constituent gases you take any volume you take this, then you divide by the total number of moles of constituent gases. So, how many moles of carbon dioxide are there? So, for example, if I want to write for a combination of CO_2 , N_2 , O_2 and let say H_2O what I will write is.

So, the mean molecular weight of dry air is sum of mass of CO_2 plus mass of N_2 plus mass of O_2 plus mass of H_2O divided by let say number of moles of CO_2 plus number of moles of O_2 plus number of moles of N_2 plus number of moles of H_2O . So, this is the idea right. So, why do you read M_d ? See, you are you again you have defined R_{star} as capital M R right. That means, if you want to calculate the specific gas sorry, the specific gas constant of dry air at various concentrations which keep changing the concentrations.

Every time you change the concentration, the value of the specific gas constant will change right. Will change, but if you want to calculate; every time you want to calculate, the specific gas constant for different combinations of these concentrations, what you can do is, you can calculate the mean molecular weight and then you if you know the universal gas constant you can do that right.


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Apparent molecular weight

- We can now define the apparent molecular weight of dry air as the total mass of constituent gases in dry air divided by the total number of moles of constituent gases.

$$M_d = \frac{\sum m_i}{\sum \frac{m_i}{M_i}}$$

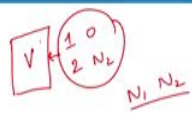
- Where, m and M represent mass and molecular weight of the i^{th} constituent.




So, simply speaking so, here small m and capital M represent the mass and the molecular weight of the i^{th} constituent. It can be made up of any number of constituent gases, you can always say that small m and capital M represent the mass and molecular weight of the i^{th} constituent right.

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Dry air



- Consider a mixture of two gases occupying a volume V and consisting of N_1 molecules of gas 1 and N_2 molecules of gas 2.
- The total pressure exerted by the mixture of gas on the wall will be the result of all the collisions i.e., by both the gases 1 and 2.



So, consider a mixture of two gases occupying volume V consisting of N_1 number of molecules of gas 1 and N_2 number of molecules of gas 2. So, for example, you consider a mixture of gases in a volume. So, the volume is fixed. So, gas number 1 let say oxygen and

gas number 2 as let say nitrogen; both of them are in this enclosure, interestingly gas number 1 has N_1 number of molecules and gas number 2 has N_2 number of molecules fine, but here we are talking about the mixture.

Since the total pressure exerted by the mixture of this gas on the walls, will be the total pressure, that is, the total momentum transfer that is happening by both the molecules. So, how do you define, I mean the pressure is the momentum transfer, right built up by the momentum transfer. So, the total pressure is a sum is a sum of pressure exerted by the oxygen atoms and pressure exerted by the nitrogen molecules, right both of them.

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Mixture of gases

- The ideal gas equation can be written as

$$p = \frac{(N_1 + N_2)kT}{V}$$

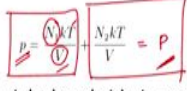
$$p = \frac{N_1kT}{V} + \frac{N_2kT}{V}$$

p_1 p_2
 due to gas 1 due to gas 2

So, ideal gas equation can now be written as p is equal to $N k T$ right. So, the total number of atoms or molecules per unit volume, the total number is N_1 plus N_2 . Now, if you split this, you will realize that the pressure the total pressure that is exerted by the mixture of gases is the sum of individual pressures. So, this you can call as P_1 and this you can call as P_2 . P_1 is due to; is due to gas number 1 and P_2 is due to gas number 2, as simple, right.

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Mixture of gases

- The ideal gas equation can be written as
$$p = \frac{(N_1 + N_2)kT}{V}$$

$$p = \frac{N_1kT}{V} + \frac{N_2kT}{V} = P$$
- Where, the first term on the right hand side is exactly the pressure exerted by gas 1 if entire volume is occupied by it alone. This is called the partial pressure of gas 1.
- The same is valid for the second term as well.
- We can say that the total pressure is the sum of two partial pressures.

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But so, the first term . So, it is the same thing that what I am speaking of. So, the first term on the right hand side is exactly the pressure exerted by the gas 1, if it is occupying the entire volume by itself right and P 2 so, here V is appearing in the denominator right.

So, if you will take this equation alone, it appears gas with number of molecules of N 1 at a temperature T occupying a volume V will exert a pressure. Similarly, you can also say this is P right. So, the total pressure is the sum of individual pressures as if the one species of gas alone is occupying the entire volume by itself right. So, that is the idea. So, this pressure is called as the partial pressure of the gas.


So, always remember partial pressure is never equal to the total pressure of the gas partial pressure is the pressure exerted by one constituent of a mixture as if, it is alone occupying the entire volume by itself right. So, this same is valid for the second term as well right like I said here right.

So, we can say that the total pressure is sum of the two partial pressures right. The most important thing of all this discussion is that, we always assume that these gases are not interacting among themselves. So, there is no chemical interaction that is happening within the mixture of gases. If it happens, in say it's a different story.

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Mixture of gases

- This expresses the Dalton's law of partial pressure: for a mixture of k components, each of which obeys the ideal gas law, the total pressure p exerted by the mixture is equal to the sum of the partial pressures which would be exerted by each gas if it alone occupied the entire volume at the temperature of the mixture, T .
- We can write that
$$p = \sum_{i=1}^k p_i$$



So, this idea is expressed by the Dalton's law of partial pressures; which states for a mixture of k component gases. Each of which obeys the ideal gas flow, the total pressure p exerted by the mixture is equal to the sum of partial pressures which would be exerted by each gas, if it alone occupied the entire volume at that temperature of the mixture of the gas right. This point is enough emphasized already, but this temperature is the mixture temperature.

So, if it is at the same temperature, but if it is occupying the same volume, but in reality, it is not the only gas which is occupying the same volume; it is a mixture of gases which is occupying the same value. So, in that case the pressure will be the sum of partial pressures. So, that is the idea. So, we can write that. So, the total pressure is the sum of partial pressures and i goes from i to k , where I also said that it's a k component gas I mean there are k different components inside the gas which are exerting this pressure right.


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Mixture of gases

- If the volume of the mixture is V and the mass and molecular weight of the i^{th} constituent are m_i and M_i respectively.
- Then for each constituent we can write that

$$p_i = \frac{R^* m_i}{M_i V} T$$

Temperature of the mixture



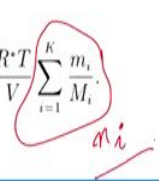
So, if the volume of the mixture is V and the total molecular weight of the i^{th} component are; total mass and the molecular weight of the i^{th} component are m_i and capital M_i . M_i is the mass how much amount of gas is present and what is the molecular weight of that species of gas say if the volume of the mixture is V and the mass and molecular weight of the i^{th} constituent or m_i and the capital M_i respectively that for each constituent.

We can write the equation. Where, we are not changing V ; we are not saying that this gas will occupy only certain volume, it is occupying the entire volume and this capital T is the temperature of the mixture you always remember this. So, this is the temperature of the mixture right.

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Dalton's law and mixture of gases

- We can apply the Dalton's law and write pressure of the mixture as

$$p = \sum_{i=1}^K \frac{R^* T_i m_i}{V M_i}$$
$$p = \frac{R^* T}{V} \sum_{i=1}^K \frac{m_i}{M_i}$$



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So, when we apply the Dalton's law, we can write the pressure of the mixture as. So, this is the sum of all the different partial pressures. So, each i will be one partial pressure right. So, here R star is a constant which is now universal gas constant. Now, your since you are accompanying with molecular weight, you use R star temperature is a constant and this is the same for all the gases. So, you pull it out. So, the pressure is now written as R star T divided by V some more i to k, m i divided by M i. So, this is what? So, this is eventually n i right.

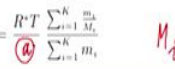
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Mean molecular weight

- The total mass of the mixture is a sum of individual masses of constituent gases

$$m = \sum_{i=1}^K m_i$$


- We can write the total pressure of the mixture as

$$p = \frac{R^* T m \sum_{i=1}^K \frac{m_i}{M_i}}{\sum_{i=1}^K m_i}$$
$$p = \frac{R^* T \sum_{i=1}^K \frac{m_i}{M_i}}{\sum_{i=1}^K m_i}$$


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So, the total mass of the mixture is a sum of individual masses of the constituents we know that. So, we can write the total pressure of the mixture of gases as total pressure. So, m is the sum right. So, we have written p is equals to R star T divided by V sum over i to k this is n divided by m . So, write n is equals to m by capital M right. So, this so, R star if you take it. So, this is this α ; this is the specific volume α .

So, p is equals to peak the pressure can be written as; in terms of the gas constant right. So, what I have done is, I have used the form of the mean molecular weight of a mixture of gases right.

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Mean molecular weight

- Now for this equation to obey the ideal gas law, it must satisfy the following

$$p = \frac{RT}{\alpha} = \frac{R^*T}{\alpha \bar{M}}$$

- Such that \bar{M} is the mean molecular weight of the mixture.
- We can write \bar{M} as $\bar{M} = \frac{\sum_{i=1}^K m_i}{\sum_{i=1}^K \frac{m_i}{M_i}}$

So, for this equation has to hold dimensionally, we will require this to be equivalent to the mean molecular weight. So, for this equation to obey the ideal gas law it must satisfy the following. So, p is equals to $R T$ by α . So, this is the original form; $p \alpha$ is equals to $R T$ right. So, then you require that this R star. So, R is the is a specific gas constant, if you put R star then the mean molecular weight should come here.

So, such that the mean molecular weight, \bar{M} is the mean molecular weight of the mixture. So, we can write \bar{M} as, mass of the individual gas constituent; total gas divided by the total number of moles right. So, this is we have already defined I mean let us say for example.

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Example

- For our planet, the lowest 25 km of the atmosphere is made up almost entirely by nitrogen (N₂), Oxygen (O₂), Argon (A) and Carbon dioxide (CO₂) (75.51%, 23.14%, 1.3%, and 0.05% by mass respectively).
- How can we calculate the mean molecular weight of the air.

So, the basic idea is this, the basic idea is the mean molecular weight of a mixture of gases having i different component gases is the sum of mass of individual gases divided by the sum of the number of moles of individual gases right. So, we take an example for our planet, let say the lowest 25 kilometers of the atmosphere is made up of almost entirely by nitrogen, oxygen, argon and carbon dioxide right.

So, N₂, O₂, argon and carbon dioxide make up nearly 100 percent of the atmosphere right. So, their percentage of occurrence is 75.51, 23.14 argon is 1.3 carbon dioxide is 0.05 by mass, not by volume or not by number; by mass. So, the of the entire mass of atmosphere 75.5 percent is nitrogen, 23.14 percent is oxygen, 1.3 percent is argon and 0.05 percent is CO₂ right.

So, now we know the molecular weights of the species right. We know, let say we can calculate what will be the; what will be the mean molecular weight of the gas, of the dry air right. How can we calculate the mean molecular weight of the air?

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Example

$$\bar{M} = \frac{m_{N_2} + m_{O_2} + m_A + m_{CO_2}}{\frac{m_{N_2}}{M_{N_2}} + \frac{m_{O_2}}{M_{O_2}} + \frac{m_A}{M_A} + \frac{m_{CO_2}}{M_{CO_2}}}$$

100 gm of dry air

$$\bar{M} = \frac{75.51 + 23.16 + 1.3 + 0.05}{\frac{75.51}{28.02} + \frac{23.14}{32.0} + \frac{1.3}{39.94} + \frac{0.05}{44.01}} \text{ g mol}^{-1}$$

$$\bar{M} = 28.97 \text{ g mol}^{-1}$$

$p\alpha = R \bar{T}$

$$\bar{M} = 0.02897 \text{ kg mol}^{-1}$$

$$R_d = R^* / \bar{M} = 287 \text{ J kg}^{-1} \text{ K}^{-1}$$

1 kg of dry air

So, let's say. So, according to the formula, mean molecular weight is let say is defined as the total mass; total mass right and the total number of moles weight by molecular weight is number of moles you take in grams let say this is for argon for CO2 and etcetera right.

So, you take one let say, you take 100 grams of dry air ok, 100 grams of dry air. So, since it is by mass. So, we can say that 75.51 grams will be nitrogen, 23.16 will be oxygen, 1.3 will be argon and 0.05 will be carbon dioxide. So, you just substitute these things. So, in the numerator you are accounting for the total mass and in the denominator, you are accounting for the total number of moles; that means, each gas has its own weight by saying that its weight is different and its number of moles are also different.

A heavier gas will not have enough number of moles to be able to influence the molecular weight in a certain way. So, if we calculate the mean molecular weight, it will be 28.97 gram per mole; in gram per mole. So, per 1 mole, the mean molecular weight it will be 28.97 right or if you say it in kgs let say 0.02897 kg per mole. So, now, if you know the mean molecular weight, you can simply calculate the specific gas constant of dry air.

So, if you want to use $P\alpha = R T$, but not $R^* T$; that means, your gas constant is specific for this combination. For this percentages, if you want to use a gas constant which is R at a given value of temperature, you can use this value; 287 Joule per kg per Kelvin. So, this is the specific gas constant of dry air. This is again as per 1 kg of for 1 kg of dry air right.

So, this is something about that the concept of mean molecular weight, how the mean molecular weight is useful to understand certain aspects about the mixture of gases and things like that right. So, from the next class, we will try to include certain humidity variables into the discussion, let say by bringing water vapor H₂O right. So, we can stop here, we will continue the discussions on atmospheric thermodynamics in the subsequent classes ok.