Course Name: An Introduction to Climate Dynamics, Variability and Monitoring

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ATMOSPHERIC GAS CONCENTRATION AND INTRODUCTION TO ATMOSPHERIC PRESSURE

Good morning class and welcome to our continuing lectures on climate dynamics, climate variability and climate monitoring. In the previous class we were discussing various aspects of atmospheric composition and we saw that even though molecules like carbon dioxide, methane, ozone etc are very small parts of the total atmosphere. In the terms of PPM levels or PPB levels, they have an outsized influence on the current anthropogenic global warming that is experienced by the world because of their ability to trap heat or absorb UV radiation, for example. So here, as we continue our discussion on global climate change, it is very important to quantify the amount of increase of these trace gases like CO2, methane, etc. And hence, I am introducing to you today certain quantitative variables that will help us track these changes and these will be used in various examples over time as the class progresses. So here the idea is that the atmosphere is a composition of multiple gases, correct? So it's a mixture.

And for the level of work that we are doing, we can assume this mixture to be a mixture of ideal gases. Now, what are ideal gases? As you may recall from your previous classes, an ideal gas is a gas for which a specific relationship between pressure of the gas, volume occupied by the gas, molar number of moles or the mass of the gas and the temperature of the gas will hold. And this specific relationship is PV equals to nRT. where p is the pressure of the gas in pascals which is newton per meter square v is the volume occupied by this gas in terms of meter cube n is the number of moles of the gas r is the ideal gas constant which is a universal constant given by 8.314 joule per mole kelvins and t is the temperature of the gas in kelvins So, ideal gases are gases for which this relation PV equals to NRT will hold under all circumstances. And for the pressures and temperatures that we are discussing in the atmosphere, the atmospheric gas composition can also be considered as a mixture of ideal gases. Now for air, the average molecular mass is 28.97 grams per mole. So if you see, it's mostly nitrogen whose molecular mass is like 28 grams per mole and some oxygen whose molecular mass is 32 grams per mole.

So the average molecular mass of air, when you consider the nitrogen is around 71% and oxygen is 28%, is coming up around 28.97 grams per mole.

$$R_{air} = \frac{R}{Mw_{air}} = 287 \frac{J}{kg.K}$$

So, here what we are doing is dividing this 8.314 joule per mole Kelvin by the molecular mass of air which is 28.97 grams per mole or 28.97 into 10 to the power minus 3 kgs per mole. So this becomes 8.314 divided by 28.97 into 10 to the power minus 3 because we are converting from grams per mole to kg per mole and this will give us the ideal gas constant of air on a mass basis as 287 joules per kg kelvin.

Using this, we can write the ideal gas law on mass basis as P into V into mass into the ideal gas constant of air into T. Note that the mass basis ideal gas constant is not universal and it is dependent on the molecular mass of the specific gas composition. So depending on what gas is this molecular mass will be changing and hence R will be changing as well on the mass basis. So this becomes a function of the molecular mass of the gas in question. So, in this context then while this is the ideal gas relationship on a molar basis, this is the ideal gas relationship on a mass basis where m is the mass of air in this case in kgs.

So, now if you divide mass by volume you get the relationship in terms of density which is more convenient to us. So, the pressure of air is equal to the density of air into the gas constant of air into the temperature of air. So, this relationship will hold regardless of which location on earth it is or how much high altitude it is. You find the density of air, you find the temperature of air and that will give you the pressure of air or vice versa. Where rho air is the density of air at the given conditions.

Okay. So, what we have said is air is an ideal gas, a mixture of ideal gases and follows either equation 3 or equation 1 depending on if you want to do it in a mole basis or a mass basis. Now, what is an air a mixture of? This is already discussed here in the table. So, it is a mixture of multiple gases. Of course, it is mostly nitrogen and oxygen, but it also contains water vapor, CO, CO2, methane, etc. in smaller quantities.

So, how do we evaluate the mole fractions of each of these components now that we have assumed air to be made up of a mixture of these gases? So, here, we use a counter i which is giving the component number in our air mixture so air is a mixture of various gas components and we are giving these gas components a counter i okay so let us assume each of these components have a molecular mass mwi so for example if nitrogen is given counter one Then molecular weight Mw1 is the molecular mass of nitrogen which is 28 grams per mole. If oxygen is counted gas number 2 in the mixture, then Mw2 is the molecular mass of oxygen which is 32 grams per mole, etc. Similarly, let each of these components have mass Mi and moles Ni in a certain mixture of air, okay. Then we can write that the total mass of air is equals to the total mass of summation of the masses of the individual components making up this air which you can again subdivide into number of moles of these components into the molecular mass of these components. Remember mass is the number of moles into the molecular mass of that component.

$$m = \sum_i m_i = \sum_i n_i Mw_i$$
$$n = \sum_i n_i$$

So, these are the two equations based on which we can evaluate the mixture mass and mixture moles. Based on this then we can define the mass fraction or mass mixing ratio.

The mass mixing ratio or mass fraction of a component i is then:-

$$y_i = \frac{m_i}{m} \qquad (6)$$

Similarly, molar mixing ratio or mole fraction

The molar mixing ratio or mole fraction of the component is:-

$$x_i = \frac{n_i}{n} \qquad (7)$$

So, we have defined two variables mass fraction and mole fraction yi and xi. Now ni and n can be written in terms of the mass and the molecular masses of the components themselves.

Mass and Molar mixing ratios are related as:-

$$y_i = \frac{Mw_i}{Mw_{air}} x_i \quad (8) \ \ where,$$
$$Mw_{air} = \sum_i Mw_i x_i \qquad (9)$$

So, mass fraction equal to molecular weight of ith component by the molecular weight of the mixture into mole fraction of that component. what is molecular weight of air? This can be taken as the summation of the product of the molecular weight and the mass fraction of the individual component.

So, molecular weight of air is mwi into xi. In the next class, we will do a few worked out examples that will help us clarify this quantities a little bit more. But here you can see we have defined the mass fraction or mass mixing ratio, the mole fraction or molar mixing ratio. We have defined the relationship between mass fraction and mole fraction as well as define the what is the molecular weight of a mixture given that we know the molecular weight of individual components and mole fraction of the individual components.

Another mixture variable is the concentration Ci which is moles per meter cube of a component i in the given mixture.

So, this concentration is also an important variable that is often used and we will use it extensively in later classes.

Often, the concentration C_i (mol/m^3) of a component 'i' is given in terms of its partial pressure p_i, which is given by,

$$p_i = \frac{n_i \hat{R} T}{\forall} = C_i \hat{R} T \quad (10)$$

Note that,

$$\frac{p_i}{p} = \frac{n_i}{n} = x_i \quad (11)$$

The partial pressure ratio of the partial pressure to total pressure is the mole fraction of the ith component.

In mass basis, the variable partial density $\rho_i = \frac{m_i}{\forall}$ is used. We can write:-

$$p_i = \rho_i R_i T \quad (12), where$$

$$R_i = \frac{\hat{R}}{Mw_i} \quad \frac{J}{kgK} \quad (13)$$

So we have also defined two important variables partial density and concentration. Another way to express the same things and we are just looking at various expressions because they will be used in later classes

Often, the component concentration in air is also given in terms of partial volume which is obtained from:-

$$\forall_i = \frac{n_i \hat{R} T}{p} \quad (14)$$

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So, the ratio of the partial volume by total volume is also the mole fraction xi, just as ratio of partial pressure by total pressure is the mole fraction xi. This is called the volume fraction, which is the same as the mass fraction.

So, wherever you see a term volume fraction being used, you can consider it numerical equal to the mole fraction xi of that component. So, these relationships help us these equations as well so for example here fraction by volume in dry air what we are giving is

Vi by V which is again same as the mole fraction Xi so all of these are basically mole fractions okay and the total mass of the component i is here what you are getting is Mi right So these are the Mi's, this is the Xi's and this is the molecular weight Mwi's for each of these components from which you can get all the other things, the concentrations, the partial pressures, the partial densities, etc. Now the next important atmospheric variable that we will discuss is atmospheric pressure and here we will particularly look at the variation of atmospheric pressure with altitude that is how pressure is changing with height. There is also an important aspect of pressure which is the variation of atmospheric pressure along the like the north-south and east-west directions. Those are very important in discussing climatic changes, weather forms, etc.

We will discuss them at a later part of the course, but here we will look at the change in pressure with altitude. Now we... All of us have a experience that as we go up into a mountain the pressure decreases, the air pressure decreases, right? So this effect is caused by the balance of the gravitational force and the pressure force.

So let's see how this happens and this relationship is called the hydrostatic balance equation. So suppose you take a small box of air at a certain height from the ground. Say the height from the ground is z and this box is a small box, differential box of width dx, length dy and height dz. So you can also call this length, width and height, whatever, dx, dy, dz. So a small differential volume element of air has been taken at a certain altitude z from the ground Now, at the bottom surface, let the pressure be P.

The pressure of air at the bottom surface is P. The pressure of air at the top surface, let us call it P minus dP. Pressure decreases a little bit, so it is P minus dP. So, the upward force that this volume of air is experiencing due to the presence of the pressure force at the bottom surface is the pressure which is force per unit area into the area of the bottom surface which is dx into dy. So, the bottom surface of this cube area is dx into dy.

So, the total upward force is P into dx into dy. Similarly, the total downward force at top surface is P minus dP into dx into dy. Because the pressure has decreased to some extent as we move upwards. Now, the mass of air here inside is the density of air into dP. volume of air which is dx dy dz into the so that is the mass of air so the mass of air

$$F_g = -gdm = -g\rho dxdydz$$

okay so the total weight of air due to gravitational force is g into this mass of air so g into rho dx dy dz so this is the net downward gravitational force that this small volume of air is is being subjected to and let us call it Fg going down.

So, it is Fg which is minus g into the differential mass of air in this volume which is minus g rho dx dy dz. and the net upward pressure force fp is the difference between pdxdy that is going upwards minus p minus dpdxdy which is pointed downwards from the top surface.

$$F_p = Pdxdy - (P - dP)dxdy = dPdxdy$$

So if you take these two you get the pressure force downward pressure force is dpdx so the upward pressure force sorry is dpdxdy so plus plus dpdxdy this is the upward pressure force. Now if we assume that this small parcel of air is stationary, air is calm so there is no movement of air at this point. If the parcel of air is stationary then this downward force due to gravity must be balancing the upward force due to pressure.

The two forces must balance when the air element is at equilibrium at the altitude z. Thus we have,

$$F_P + F_g = 0$$

$$\text{or,} \quad dP = -g\rho dz$$

$$\text{or,} \quad g = -\frac{1}{\rho}\frac{dP}{dz} \quad (hydrostatic\ balance)$$

dp dz is the rate of change of pressure with altitude. Okay. So, what you get is basically dp dz is equals to minus rho into g that the rate of change of pressure with altitude as we go up is equals to minus rho into g. It's negative so pressure is decreasing with altitude and the amount of the slope of this decrease is the density of air at that point into the gravitational acceleration g. So this is called the hydrostatic balance relation, a very important relation in terms of looking at how pressure is changing with altitude.

So dp dz is the pressure fall of gradient with altitude Air can be assumed to be an ideal gas and hence the ideal gas relation P equals to rho RT applies to it. So we must have rho equals to p by RT. So here then the ideal gas relationship becomes important because p is equals to rho RT for air. So rho is p by RT.

R is here the gas constant on a mass basis. Universal gas constant by molecular mass of air. So this rho can now be put here.

$$H = \frac{RT}{g} \quad (metres) \quad (17)$$

we write the variable RT by g as the scale height h because its units are in meters. So this you can evaluate yourself.

This is joule per kg kelvin and joule is Newton meter. T is temperature, G is meter per second square. So, you do the unit evaluations properly and you will get the scale height

H as RT by G and its unit is meters. So, once you put the scale height H in this expression, the final expression that you get is this expression here. dp by p is equals to minus dz by h. So, we put dp by p on this side and dz on this side and h becomes RT by g.

So, this basically becomes minus g by RT dz. So what we have done here, we have replaced the density rho by P by RT and then rearranged the variables and expressed this RT by G as a scale height variable called H. So we are getting this expression here.

Using the above expressions, the hydrostatic balance equation (1) can be written as,

$$\frac{dP}{P} = -\frac{dz}{H} \quad (18)$$

Now, two important points. Firstly, the temperature is not constant as we move up from the sea floor towards the top of the troposphere or stratosphere. That we have already seen, correct? We have seen that the temperature is changing significantly with altitude.

So, you see a large variation of temperature with altitude. So, this expression cannot be integrated very easily because you also need to know how the temperature is a variable of Z. That has to be put into this expression. A very simple assumption that we can do and we will expand on further work in the next set of classes that we can put a mass average temperature of the atmosphere. So, you basically integrate And take the mass average temperature.

So, it is basically like integral of T dm by m. That is you are averaging per unit mass how much temperature is and averaging it together. And you get a mass average temperature of the vertical column of the atmosphere. This mass average temperature is T0 of equal to 260 Kelvin. So, we can assume kind of an average scale height H0 as R into T0 by g, where T0 is 260 Kelvin.

If you do that, then H0 becomes around 7.6 kilometers. So, what we have done? In general, this temperature is changing with altitude. But we can take a mass average temperature of an entire column of atmosphere from the sea level to the top of say the exosphere and the mass average temperature becomes 260 kelvins and we can use that to get a approximate mass average scale height H0 of 7.6 kilometers. If we take H0 as a constant, then this expression becomes very easy to integrate and you get P equals to Ps into exponential minus z by H0.

So, when you integrate all of this, you get the final expression as here.

$$P = P_s \exp\left(-\frac{z}{H_o}\right) \quad (19)$$

The pressure at any altitude z is equals to the pressure at the sea level into exponential minus z by H0.

So here Z is the altitude at which this pressure is being measured. So here basically what you write is P at a given altitude Z equals to P at the sea level which is taken to be approximately 1.01325 into 10 to the power 5 Pascals which is the standard one atmospheric pressure at sea level and this exponential minus Z by H0. Remember H0 is 7.6 kilometers. So Z you can also take in terms of kilometers. So what you get out of this is you can plot this expression here and this has been plotted here with terms of altitude. Here pressure is hectopascals which is 100 pascals. So here pressure is expressed in terms of 100 pascals in the x-axis and the altitude is in kilometers. And you can see the pressure is an exponentially decaying function. with altitude as you would expect from this relation.

$$P = P_s \exp\left(-\frac{z}{H_o}\right) \qquad (19)$$

So, we will stop here today. We will continue this discussion and expand upon cases where temperature is not constant, how to deal with those things. So, those things we will look into next week. So, thank you for listening and see you again in the next class. Thank you.