## M.Sc. in Meteorology

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Part 2
Atmospheric Thermodynamics

## Atmospheric Thermodynamics

Thermodynamics plays an important role in our quantitative understanding of atmospheric phenomena, ranging from the smallest cloud microphysical processes to the general circulation of the atmosphere.

The purpose of this section of the course is to introduce some fundamental ideas and relationships in thermodynamics and to apply them to a number of simple, but important, atmospheric situations.

The course is based closely on the text of Wallace 83 Hobbs

## Outline of Material

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- 1 The Gas Laws
- 2 The Hydrostatic Equation
- 3 The First Law of Thermodynamics
- 4 Adiabatic Processes
- 5 Water Vapour in Air
- 6 Static Stability
- 7 The Second Law of Thermodynamics


## The Kinetic Theory of Gases

The atmosphere is a gaseous envelope surrounding the Earth. The basic source of its motion is incoming solar radiation, which drives the general circulation.

To begin to understand atmospheric dynamics, we must first understand the way in which a gas behaves, especially when heat is added are removed. Thus, we begin by studying thermodynamics and its application in simple atmospheric contexts.

## The Kinetic Theory of Gases

The atmosphere is a gaseous envelope surrounding the Earth. The basic source of its motion is incoming solar radiation, which drives the general circulation.

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Fundamentally, a gas is an agglomeration of molecules. We might consider the dynamics of each molecule, and the interactions between the molecules, and deduce the properties of the gas from direct dynamical analysis. However, considering the enormous number of molecules in, say, a kilogram of gas, and the complexity of the inter-molecular interactions, such an analysis is utterly impractical.

We resort therefore to a statistical approach, and consider the average behaviour of the gas. This is the approach called the kinetic theory of gases. The laws governing the bulk behaviour are at the heart of thermodynamics. We will not consider the kinetic theory explicitly, but will take the thermodynamic principles as our starting point.

## The Gas Laws

The pressure, volume, and temperature of any material are related by an equation of state, the ideal gas equation. For most purposes we may assume that atmospheric gases obey the ideal gas equation exactly.

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The ideal gas equation may be written

$$
p V=m R T
$$

Where the variables have the following meanings:

$$
\begin{aligned}
p & =\text { pressure }(\mathbf{P a}) \\
V & =\text { volume }\left(\mathbf{m}^{3}\right) \\
m & =\text { mass }(\mathrm{kg}) \\
T & =\text { temperature }(\mathbf{K}) \\
R & =\text { gas constant }\left(\mathbf{J ~ K}^{-1} \mathbf{k g}^{-1}\right)
\end{aligned}
$$

Again, the gas law is:

$$
p V=m R T
$$

The value of $R$ depends on the particular gas. For dry air, its value is $R=287 \mathbf{J ~ K}^{-1} \mathbf{k g}^{-1}$.

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Exercise: Check the dimensions of $R$.

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Exercise: Check the dimensions of $R$.
Since the density is $\rho=m / V$, we may write

$$
p=R \rho T
$$

Defining the specific volume, the volume of a unit mass of gas, as $\alpha=1 / \rho$, we can write

$$
p \alpha=R T
$$

## Special Cases

Boyle's Law: We may write

$$
V=\frac{m R T}{p}
$$

For a fixed mass of gas at constant temperature, $m R T$ is constant, so volume is inversely proportional to pressure:

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$$

Charles Law: We may write

$$
V=\left(\frac{m R}{p}\right) T
$$

For a fixed mass of gas at constant pressure, $m R / p$ is constant, so volume is directly proportional to temperature:
$V \propto T$.

## Avogadro's Hypothesis

One mole (mol) of a gas is the molecular weight in grams. One kilomole (kmol) of a gas is the molecular weight in kilograms. For example, the molecular weight of nitrogen $N_{2}$ is 28 (we ignore the effects of isotopic variations). So:

One mole of $N_{2}$ corresponds to 28 g
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One kilomole of $N_{2}$ corresponds to 28 kg
According to Avogadro's Hypothesis, equal volumes of different gases at a given temperature and pressure have the same number of molecules; or, put another way, gases with the same number of molecules occupy the same volume at a given temperature and pressure.

The number of molecules in a mole of any gas is a universal constant, called Avogadro's Number, $N_{A}$. The value of $N_{A}$ is $6.022 \times 10^{23}$. So:

28 g of nitrogen contains $N_{A}$ molecules of $N_{2}$ 28 kg contains $10^{3} \times N_{A}$ molecules.

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For a gas of molecular weight $M$, with mass $m$ (in kilograms) the number $n$ of kilomoles is

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

So, we use $m=n M$ in the gas law to write it

$$
p V=n(M R) T
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$$

By Avogadro's hypothesis, equal volumes of different gases at a given temperature and pressure have the same number of molecules. Therefore, the value of $M R$ is the same for any gas. It is called the universal gas constant, denoted:

$$
R^{*}=M R=8.3145 \mathbf{J ~ K}^{-1} \mathbf{~ m o l}^{-1}=8314.5 \mathbf{J ~ K}^{-1} \mathbf{k m o l}^{-1} .
$$

Then the gas law may be written in the form normally found in texts on chemistry:

$$
p V=n R^{*} T
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with $n$ the number of moles of gas and $R^{*}=8.3145 \mathbf{J ~ K}^{-1} \mathbf{m o l}^{-1}$.

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with $n$ the number of moles of gas and $R^{*}=8.3145 \mathbf{J ~ K}^{-1} \mathbf{m o l}^{-1}$.
The gas constant for a single molecule of a gas is also a universal constant, called Boltzmann's constant, $k$. Since the gas constant $R^{*}$ is for $N_{A}$ molecules (the number in a kilomole), we get

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k=\frac{R^{*}}{N_{A}}
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Now, for a gas containing $n_{0}$ molecules per unit volume, the equation of state is

$$
p=n_{0} k T
$$

## Virtual Temperature

The mean molecular weight $M_{d}$ of dry air is about 29 (average of four parts $\mathrm{N}_{2}$ (28) and one part $\mathrm{O}_{2}(32)$ ).

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Thus, the mean molecular weight, $M_{m}$, of moist air, which is a a mixture of dry air and water vapour, is less than that, $M_{d}$, of dry air and more than that of water vapour:

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M_{v}<M_{m}<M_{d}
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The gas constant for water vapour is larger than that for dry air:

$$
R_{d}=\frac{R^{*}}{M_{d}}, \quad \text { and } \quad R_{v}=\frac{R^{*}}{M_{v}}
$$

so that

$$
M_{v}<M_{d} \quad \Longrightarrow \quad R_{v}>R_{d}
$$

The numerical values of $R_{d}$ and $R_{v}$ are as follows:

$$
R_{d}=\frac{R^{*}}{M_{d}}=287 \mathbf{J ~ K}^{-1} \mathbf{k g}^{-1}, \quad R_{v}=\frac{R^{*}}{M_{v}}=461 \mathbf{J ~ K}^{-1} \mathbf{k g}^{-1}
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We define the ratio of these as:

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\varepsilon \equiv \frac{R_{d}}{R_{v}}=\frac{M_{v}}{M_{d}} \approx 0.622
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For moist air, which is a mixure of dry air and water vapour, the mean molecular weight $M_{m}$, and therefore also the gas 'constant' $R_{m}$, depends on the amount of moisture in the air.

It is inconvenient to use a gas 'constant' which varies in this way. It is simpler to retain the constant $R=R_{d}$ for dry air, and to use a modified temperature, $T_{v}$, in the ideal gas equation. We call this the virtual temperature.

## Mixing Ratio

Let's consider a fixed volume $V$ of moist air at temperature $T$ and pressure $p$ which contains a mass $m_{d}$ of dry air and a mass $m_{v}$ of water vapour. The total mass is $m=m_{d}+m_{v}$. The mixing ratio is defined by

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In middle latitudes, $w$ is typically a few grams per kilogram. In the tropics it can be greater than $20 \mathrm{~g} \mathrm{~kg}^{-1}$. If there is no evapouration or condensation, the mixing ratio is a conserved quantity.

## Mixing Ratio and Vapour Pressure

By the ideal gas law, the partial pressure pressure exerted by a constituent of a mixture of gases is proportional to the number of kilomoles of the constituent in the mixture. Thus:

$$
\begin{aligned}
p_{d} & =n_{d} R^{*} T \quad \text { dry air } \\
e & =n_{v} R^{*} T \quad \text { water vapour } \\
p & =n R^{*} T \quad \text { moist air }
\end{aligned}
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where $p_{d}$ is the pressure due to dry air, $e$ the pressure due to water vapour and $p$ the total pressure.

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where $p_{d}$ is the pressure due to dry air, $e$ the pressure due to water vapour and $p$ the total pressure.
Therefore,

$$
\frac{e}{p}=\frac{n_{v}}{n}=\frac{n_{v}}{n_{v}+n_{d}}=\frac{m_{v} / M_{v}}{m_{v} / M_{v}+m_{d} / M_{d}}
$$

Dividing by $M_{v} / m_{d}$, this gives

$$
\frac{e}{p}=\frac{w}{w+\varepsilon}
$$

Problem: If the mixing ratio is $5.5 \mathrm{~g} \mathrm{~kg}^{-1}$, and the total pressure is $p=1026.8 \mathrm{hPa}$, calculate the vapour pressure.

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Solution: We have

$$
e=\left(\frac{w}{w+\varepsilon}\right) p \approx \frac{w}{\varepsilon} p
$$

where $\varepsilon=0.622$. Substituting $w=5.5 \mathrm{~g} \mathrm{~kg}^{-1}=0.0055 \mathrm{~g} \mathrm{~g}^{-1}$, we find that $e=9 \mathbf{h P a}$.

## Virtual Temperature

The density of the mixture of air and water vapour is

$$
\rho=\frac{m_{d}+m_{v}}{V}=\rho_{d}+\rho_{v}
$$

where $\rho_{d}$ is the value the density would have if only the mass $m_{d}$ of dry air were present and $\rho_{v}$ is the value the density would have if only the mass $m_{v}$ of water vapour were present.

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We apply the ideal gas law to each component:

$$
\begin{aligned}
p_{d} & =R_{d} \rho_{d} T \\
e & =R_{v} \rho_{v} T
\end{aligned}
$$

where $p_{d}$ and $e$ are the partial pressures exerted by the dry air and water vapour respectively.

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p=p_{d}+e .
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\rho=\rho_{d}+\rho_{v} & =\frac{p_{d}}{R_{d} T}+\frac{e}{R_{v} T} \\
& =\frac{p-e}{R_{d} T}+\frac{R_{d}}{R_{v}} \frac{e}{R_{d} T} \\
& =\frac{p}{R_{d} T}-\frac{e}{R_{d} T}+\varepsilon \frac{e}{R_{d} T} \\
& =\frac{p}{R_{d} T}\left[1-\frac{e}{p}(1-\varepsilon)\right] .
\end{aligned}
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& =\frac{p}{R_{d} T}\left[1-\frac{e}{p}(1-\varepsilon)\right] .
\end{aligned}
$$

We may write this equation as

$$
p=R_{d} \rho T_{v}
$$

where the virtual temperature $T_{v}$ is defined by

$$
T_{v}=\frac{T}{1-(e / p)(1-\varepsilon)}
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The great advantage of introducing virtual temperature is that the total pressure and total density of the mixture are related by the ideal gas equation with the gas constant the same as that for dry air, $R_{d}$.

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The virtual temperature is the temperature that dry air must have in order to to have the same density as the moist air at the same pressure. Note that the virtual temperature is always greater than the actual tempeature:

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T_{v} \geq T
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$$
T_{v} \geq T
$$

Typically, the virtual temperature exceeds the actual temperature by only a few degrees.

## Approximate Expressions for $T_{v}$

We can assume that $e \ll p$ and also that $w$ is small. By the binomial theorem,

$$
\frac{1}{1-(e / p)(1-\varepsilon)} \approx 1+(e / p)(1-\varepsilon)
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and the virtual temperature is

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T_{v} \approx T\left[1+\frac{e}{p}(1-\varepsilon)\right] .
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Now substituting for $e / p$, we get

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$$
\left[1+\frac{e}{p}(1-\varepsilon)\right]=\left[1+\frac{w}{w+\varepsilon}(1-\varepsilon)\right]
$$

But we assume that $w \ll \varepsilon$, so we get

$$
\left[1+\frac{w}{w+\varepsilon}(1-\varepsilon)\right] \approx\left[1+\frac{1-\varepsilon}{\varepsilon} w\right]
$$

Again,

$$
\left[1+\frac{w}{w+\varepsilon}(1-\varepsilon)\right] \approx\left[1+\frac{1-\varepsilon}{\varepsilon} w\right]
$$

Since $\varepsilon=0.622$ we have $(1-\varepsilon) / \varepsilon=0.608$. Thus,

$$
T_{v} \approx T[1+0.608 w]
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Problem: Calculate the virtual temperature of moist air at $30^{\circ} \mathrm{C}$ having a mixing ratio of $20 \mathrm{~g} \mathrm{~kg}^{-1}$.

Again,

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\left[1+\frac{w}{w+\varepsilon}(1-\varepsilon)\right] \approx\left[1+\frac{1-\varepsilon}{\varepsilon} w\right]
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Problem: Calculate the virtual temperature of moist air at $30^{\circ} \mathrm{C}$ having a mixing ratio of $20 \mathrm{~g} \mathrm{~kg}^{-1}$.
Solution: First, $T=30+273=303 \mathbf{K}$ and $w=20 \mathbf{g ~ k g}^{-1}=$ $0.02 \mathrm{~g} \mathrm{~g}^{-1}$. Then

$$
T_{v} \approx 303[1+0.608 \times 0.02]=306.68 \mathrm{~K}
$$

So, the virtual temperature is $(306.68-273)=33.68^{\circ} \mathbf{C}$, an elevation of $3.68^{\circ} \mathrm{C}$ above the actual temperature.

End of $\S 2.1$

