# UCF Physics: AST 6165: <br> Planetary Atmospheres Lecture Notes 

Prof. Joseph Harrington<br>Planetary Sciences Group<br>Department of Physics<br>University of Central Florida<br>Orlando, Florida 32816<br>jh@physics.ucf.edu<br>(c)2008-2020 Joseph Harrington. All rights reserved.

4 May 2020

## Acknowledgements

Csaba Palotai for guest lectures and many discussions on dynamics and moisture.
Katia Matcheva for guest lectures in the first two iterations of this course.
Sara Sullivan and Jay Harrington for their love and support during the first iteration of the course.

## Contents

Acknowledgements ..... i
1 Introduction ..... 1
1.1 Check in: : - :, 10 min ..... 1
1.2 Welcome: : -:, 5 min ..... 1
1.3 What's an Atmosphere?: : - :, 15 min ..... 2
1.4 Course Materials: : - :, 30 min ..... 3
1.5 Introduction: Physical System: :-:, 15 min ..... 3
1.6 Introduction: Models and Observation: : - :, 10 min ..... 4
1.7 Check in: : — :, 5 min ..... 4
1.8 Topic Picks: : - :, 15 min ..... 4
1.9 Global Mean Temperature I, Airless: : - :, 20 min ..... 4
1.10 Global Mean Temperature II, Atmosphere: : - :, 30 min ..... 6
1.11 Global Warming: : - :, 20 min ..... 8
2 Thermodynamics ..... 9
2.1 Check in: : - :, 5 min ..... 9
2.2 HW1 Discussion: : - :, 20 min ..... 9
2.3 Meaning and Forms of the Ideal Gas Law: : - :, 20 min ..... 9
2.4 Isothermal Structure: : - :, 10 min ..... 10
2.5 Isothermal Examples and Intuition: : - :, 10 min ..... 11
2.6 Lapse Rate: : - :, 10 min ..... 14
2.7 Check in: : - :, 5 min ..... 14
2.8 Atmospheric Structure: : - :, 15 min ..... 15
2.9 Potential Temperature: : - :, 30 min ..... 16
3 Oscillation ..... 19
3.1 Check in: : — :, 0 min ..... 19
3.2 Adiabatic Lapse Rate: : - :, 25 min ..... 19
3.3 Live Examples: : - :, 15 min ..... 20
3.4 Schedule Presentations: : - :, 10 min ..... 21
3.5 Oscillation and Convection: : - :, 50 min ..... 21
3.6 Live Example: : - :, 20 min ..... 22
3.7 Cloud Forms: : - :, 10 min ..... 22
3.8 Atmospheric Energy: : - :, 10 min ..... 22
3.9 Available Potential Energy: : - :, 5 min ..... 23
3.10 How Do We Measure Motions?: : - :, 10 min ..... 24
3.11 HW 3: : - :, 35 min ..... 24
3.12 Moisture in the Atmosphere: :-:, 5 min ..... 25
3.13 Cloud and Precipitation Formation: :-:, 10 min ..... 26
3.14 How do we quantify moisture?: : - :, 15 min ..... 26
3.15 Phase Changes: : - :, 15 min ..... 28
3.16 Saturated Adiabatic Lapse Rate (SALR): : - :, 10 min ..... 31
3.17 Diagrams: : - :, 15 min ..... 31
3.18 Presentations: : - :, 45 min ..... 32
4 Radiation Basics ..... 33
4.1 Check in: : - :, 6 min ..... 33
4.2 Landscape: : - :, 5 min ..... 33
4.3 Atmospheric Radiation Concepts: : - :, 15 min ..... 33
4.4 Gaining and Losing Photons: : - :, 15 min ..... 34
4.5 Thermal Radiation: : - :, 20 min ..... 35
4.6 Radiometric Quantities: : - :, 15 min ..... 36
5 Radiative Transfer Equation ..... 39
5.1 Check in: : - :, 5 min ..... 39
5.2 Local Thermodynamic Equillibrium (LTE): : - :, 5 min ..... 39
5.3 Back in Black: : - :, 10 min ..... 40
5.4 Extinction and Emission: : - :, 30 min ..... 40
5.5 Student Report: : - :, 25 min ..... 41
5.6 HW4 Discussion: : - :, 45 min ..... 41
6 Spectral Line Formation ..... 43
6.1 Check in: : - :, 5 min ..... 43
6.2 Planck as Source Function: : - :, 5 min ..... 43
6.3 Diffuse Approximation: : - :, 10 min ..... 43
6.4 Molecular Quantum States: :- :, 15 min ..... 44
7 Spectral Line Shapes ..... 45
7.1 Check in: : — :, 5 min ..... 45
7.2 Line Shapes: : - :, 5 min ..... 45
7.3 Collisional (Natural) Broadening: : - :, 20 min ..... 45
7.4 Doppler Broadening: : - :, 15 min ..... 46
7.5 Transmittance, Bands, Blending: : - :, 25 min ..... 47
7.6 1D Atmospheric Radiative Transfer - Setup: : - :, min ..... 48
7.7 Spectra of Some Key Gases: : - :, 10 min ..... 48
7.8 3D Atmospheric Spectra: : - :, 10 min ..... 48
7.9 Transmission and Emission Observations: :- :, min ..... 49
7.10 Retrieval: : - :, 15 min ..... 49
8 Atmospheric Dynamics ..... 51
8.1 Material Derivative: : - :, 15 min ..... 51
8.2 Conservation of Mass, Continuity Equation: :- :, 20 min ..... 52
8.3 Conservation of Momentum: Navier-Stokes Equation: :- :, 20 min ..... 53
8.4 Rotating Frames of Reference: : - :, 20 min ..... 54
8.5 Energy Equation: : - :, 20 min ..... 54
8.6 Governing Equation Summary: : - :, 20 min ..... 55
8.7 Spherical Coordinates: : - :, 10 min ..... 55
8.8 Approximations to the Spherical Equations: : - :, 10 min ..... 56
8.9 Scale Analysis: : - :, 10 min ..... 56
8.10 Geostrophic Flow: : - :, 10 min ..... 57
8.11 Thermal Wind Equations: : - :, 10 min ..... 58
8.12 HW8: : - :, 40 min ..... 58
8.13 Gradient-Wind Balance: : - :, 5 min ..... 58
8.14 Vorticity: : - :, 25 min ..... 59
8.15 Pressure Coordinates and Geopotential: : - :, 20 min ..... 61
9 Chemical Reaction Rates ..... 63
9.1 Check in: : - :, 5 min ..... 63
9.2 Chemistry and Physics: :-:, 5 min ..... 63
9.3 Questions: : - :, 5 min ..... 63
9.4 What's Easy?: : - :, 5 min ..... 64
9.5 What's Hard?: : - :, 5 min ..... 64
9.6 Our Approach: : - :, 5 min ..... 65
9.7 Thermodynamics: : - :, 10 min ..... 65
9.8 Ozone Example: : - :, 5 min ..... 66
9.9 Unimolecular Rate Constant: : - :, 15 min ..... 66
9.10 Bimolecular Rate Constant: : - :, 5 min ..... 67
9.11 Simultaneous Loss Reactions: : - :, 5 min ..... 67
9.12 Simultaneous Loss and Gain Reactions: :-:, 5 min ..... 67
10 Chemical Reactions ..... 69
10.1 Check in: : - :, 5 min ..... 69
10.2 Physics of Reactions: : - :, 15 min ..... 69
10.3 Collision Theory: : - :, 20 min ..... 70
10.4 Photodissociation: : - :, 20 min ..... 70
10.5 Equilibrium Chemistry on Giant Planets: : - :, 25 min ..... 71

## Chapter 1

## Introduction

## Pre-Class:

Contact guest lecturers, confirm what they'll do and when
Update schedule and syllabus
Prepare class Canvas
Copy handouts
Copy handouts, demos, visuals to Canvas
Handouts:
Syllabus
Schedule
HW1

### 1.1 Check in: : - :, 10 min

- Introductions


### 1.2 Welcome: : - :, $5 \mathbf{m i n}$

- I'm (name) and this is AST 6165 Planetary Atmospheres.
- We will be video-recording the lectures and Joe will post them online.
- The lectures, homework, handouts, solutions, videos, etc. are all on WebCourses.
- Please bring a computer to class so you can follow along in the lecture notes and do web searches online. Doing other activities in class (email, texting, homework for this or other classes) is not permitted!
- There is quite a bit of calculating in the class, but you can do most of it in a spreadsheet, if you're good with spreadsheets. Solutions to homework are mostly in Python, but you may use any means of calculating.
- The textbook is Andrews. Reading is assigned on the homework. Please read Chapter 1.
- Homework 1 is posted online.


### 1.3 What's an Atmosphere?: : - :, 15 min

- Most of us don't think about the atmosphere as a physics problem. It's just there. We get intuition about it from weather reports on the news and our own experience.
- Most of that experience says, "You never know what's going to happen."
- But in fact, mostly it's predictable:
- The air doesn't suddenly freeze and fall on the surface with a thud.
- The temperature stays in the same range, which we think of as wide, but it mostly stays within about a $15 \%$ range on an absolute scale.
- Winds are only rarely above $100 \mathrm{~km} / \mathrm{h}$.
- The pressure and temperature pretty reliably drop as you go up a mountain.
- We care about the small changes, which are hard to predict, because of how they affect our bodies, which are fragile. But the big picture is pretty stable.
- But there are many kinds of atmospheres, and many are not at all like the Earth...
- (spend about ONE minute on each of these; diagram and emphasize source, sinks, dominant physics, differences)
- Terrestrial planet (sources and sinks)
- Giant planet (diagram cross-section)
- Sun/Star (note addition of plasma and magnetic fields)
- Thin (dominated by source and sink effects, e.g., Io)
- Extended/escaping (all atmospheres escape)
- Comet (ultimate escaping atmosphere, super/subsonic expansion boundary)
- Planet-forming (protoplanetary) disk
- Where does an atmosphere end? Where the next effect is stronger.
- Optional semester assignment: photograph/video weird atmospheric phenomenon, understand it, present it. Talk to jh first.


### 1.4 Course Materials: : - :, $\mathbf{3 0} \mathbf{m i n}$

- Syllabus
- Text
- Assignments
- Topics
- Computing
- Office hours
- Alternate texts - Ingersoll, Pierrehumbert, Fegley and Lodders, list at end of Ch. 1


### 1.5 Introduction: Physical System: : - :, 15 min

- Atmosphere is a mixture of ideal gases
- $\mathrm{N}_{2}, \mathrm{O}_{2}$ dominate
- Traces $\mathrm{CO}_{2}, \mathrm{O}_{3}, \mathrm{H}_{2} \mathrm{O}$ have important roles
- Forced by Sun, interact w/ land and oceans
- Radiation scattered by gas, reflected by clouds, absorbed
- Radiation emitted
- Photochemistry
- Hydrostatic $H \sim 7-8 \mathrm{~km}$, even if non-isothermal
- $\Rightarrow$ density stratification
- Restoring force from stratification $\Rightarrow$ stable
- Heat moves: thermo
- Heat exchanged between surface and atmosphere through evaporation
- Macroscopic physics for $T \& P$, continuum approximation
- Weather is complex!
- Coriolis effect $\sim$ horizontal pressure gradients
- Flows circulate along isobars
- Buoyancy $\Rightarrow$ gravity (not GR!) waves
- Coriolis $\Rightarrow$ Rossby waves
- Ozone chemistry, heating, shielding, ozone hole
- Precipitation
- Global climate change


### 1.6 Introduction: Models and Observation: : - :, 10 min

- Remote sensing (imaging, radar, lidar) is the main way we get atmospheric data
- Very interacting system
- Few experiments possible
- Observe, sort data, hypothesis, observational test, model
- Simple $\Rightarrow$ complex model heirarchy
- Simple (analytical) models produce intuition
- Complex models may even agree w/ data


## Surface Temperature and Global Warming

### 1.7 Check in: : — :, $5 \mathbf{m i n}$

- Questions?
- Who has the book?


### 1.8 Topic Picks: : — :, 15 min

See handout. Talks start in 4th week of class.

### 1.9 Global Mean Temperature I, Airless: : - :, 20 min

- We'll start with the most basic question about a gas: temperature
- Observation: Mean surface $T=288 \mathrm{~K}$
- 2 calculations, one airless, one with atmosphere
- airless would apply to "optically thick" layer high in atmosphere
- "Solar constant" $F_{\mathrm{s}}=L_{\odot} / 4 \pi a^{2}=4 \pi R_{\odot}^{2} \sigma T_{\odot}^{4} / 4 \pi a^{2}=1370 \mathrm{~W} / \mathrm{m}^{2}$
- Note: Sun, planetary surfaces, asteroids, etc. absorb all non-reflected light and emit (nearly) as blackbodies: $F_{\text {surf }}=\sigma T^{4}$. This is a surface flux. More later in course.
- If sun as big as Earth's orbit and $L_{\odot}$ same, what is $F_{s}$ ?
- If know $L$ and know $R$ of sun or planet, know $T$ !
- Earth punches a hole w/ area $\pi R^{2}$ in solar radiation
- Gets $F_{\mathrm{s}} \pi R^{2}$ total power [W]
- Good to do a lot of unit checking in course. Many things in denominator.
- Bond albedo (reflectivity), $A=0.3$
- Keeps $P_{\text {in }}=(1-A) F_{\mathrm{s}} \pi R^{2}$
- Emits $P_{\text {out }}=4 \pi R^{2} \sigma T^{4}$
- $\sigma=5.67 \times 10^{-8} \mathrm{~W} \mathrm{~m}^{-2} \mathrm{~K}^{-4}$
- Solve:

$$
\begin{equation*}
T=\left(\frac{(1-A)}{4} \frac{F_{\mathrm{s}}}{\sigma}\right)^{1 / 4}=255 \mathrm{~K} \tag{1.1}
\end{equation*}
$$

- Not 288 K
- The average flux delivered to the atmosphere (box \& save):

$$
\begin{equation*}
F_{0}=\frac{(1-A)}{4} F_{\mathrm{s}} \approx 240 \mathrm{~W} \mathrm{~m}^{-2} \tag{1.2}
\end{equation*}
$$

### 1.10 Global Mean Temperature II, Atmosphere: : - :, $\mathbf{3 0} \mathbf{m i n}$



- Add a monolayer atmosphere (figure)
- $T_{\mathrm{a}}=$ atmospheric temperature
- $T_{\mathrm{g}}=$ ground temperature
- $F_{0}=$ non-reflected (input) solar flux
- $\mathcal{T}_{\mathrm{s}}=$ transmittance of atmosphere
- $1-\mathcal{T}_{\mathrm{s}}=$ absorptance of atmosphere $=$ emittance $($ Kirchhoff $)$
- non-black bodies emit as $F=(1-\mathcal{T}) \sigma T^{4}$
- $F_{\mathrm{a}}=$ flux emitted from atmosphere $=\left(1-\mathcal{T}_{\mathrm{s}}\right) \sigma T_{a}^{4}$
- $\mathcal{T}_{s}$ is short (visible)-wavelength transmittance $\approx 0.9$
- $\mathcal{T}_{t}$ is long (IR)-wavelength transmittance $\approx 0.2$
- $F_{\mathrm{g}}=$ flux emitted from ground $=\sigma T_{\mathrm{g}}^{4}$
- Atmosphere transmits $\mathcal{T}_{\mathrm{s}}$ downward but $\mathcal{T}_{\mathrm{t}}$ upward
- Most of the flux down is in the visible, but most up is in IR
- Balance fluxes at ground-atmosphere boundary and at top of atmosphere
- Balance fluxes at top of atmosphere: $F_{0}=F_{\mathrm{a}}+\mathcal{T}_{\mathrm{t}} F_{\mathrm{g}}$
- Balance fluxes at ground-atmosphere boundary: $F_{\mathrm{g}}=F_{\mathrm{a}}+\mathcal{T}_{\mathrm{s}} F_{0}$
- Eliminate $F_{\mathrm{a}}$, so (box \& save)

$$
\begin{equation*}
F_{\mathrm{g}}=\sigma T_{\mathrm{g}}^{4}=F_{0} \frac{1+\mathcal{T}_{s}}{1+\mathcal{T}_{t}} \tag{1.3}
\end{equation*}
$$

- $F_{\mathrm{g}} \approx 1.6 F_{0}$
- $T_{\mathrm{g}}^{4} \approx 1.6 T_{0}^{4}$
- $T_{\mathrm{g}} \approx 1.6^{1 / 4} T_{0}=1.6^{1 / 4} 255 \mathrm{~K}=287 \mathrm{~K}$
- A good match given reasonable transmittances
- Temperature of atmosphere:

$$
\begin{equation*}
F_{\mathrm{a}}=\left(1-\mathcal{T}_{t}\right) \sigma T_{a}^{4}=F_{0} \frac{1+\mathcal{T}_{s} \mathcal{T}_{t}}{1+\mathcal{T}_{t}} \tag{1.4}
\end{equation*}
$$

- $T_{\mathrm{a}} \approx 245 \mathrm{~K}$
- Real atmosphere is much more complex!


### 1.11 Global Warming: : - :, 20 min

- Note: Greenhouse effect is not controversial. Warming is. Here's why.
- Above, we derived:
- The average flux delivered to the atmosphere:

$$
\begin{equation*}
F_{0}=\frac{(1-A)}{4 f} F_{\mathrm{s}} \approx 240 \mathrm{~W} \mathrm{~m}^{-2} \tag{1.5}
\end{equation*}
$$

- The average flux at the ground:

$$
\begin{equation*}
F_{\mathrm{g}}=\sigma T_{\mathrm{g}}^{4}=F_{0} \frac{1+\mathcal{T}_{s}}{1+\mathcal{T}_{t}} \tag{1.6}
\end{equation*}
$$

- If absorbing gas amount increases, both $\mathcal{T}$ s increase.
- Combine boxed equations:

$$
\begin{equation*}
\sigma T_{\mathrm{g}}^{4}=\frac{(1-A)}{4 f} F_{\mathrm{s}} \frac{1+\mathcal{T}_{s}}{1+\mathcal{T}_{t}} \tag{1.7}
\end{equation*}
$$

- Take log and then differentiate (with respect to $x$ !)

$$
\begin{gather*}
\ln \sigma+4 \ln T_{\mathrm{g}}=-\ln 4 f+\ln (1-A)+\ln F_{\mathrm{s}}+\ln \left(1+\mathcal{T}_{s}\right)-\ln \left(1+\mathcal{T}_{t}\right)  \tag{1.8}\\
4 \frac{\mathrm{~d} T_{\mathrm{g}}}{T_{\mathrm{g}}}=+\frac{\mathrm{d} \mathcal{T}_{s}}{\left(1+\mathcal{T}_{s}\right)}-\frac{\mathrm{d} \mathcal{T}_{t}}{\left(1+\mathcal{T}_{t}\right)}-\frac{\mathrm{d} A}{(1-A)} \tag{1.9}
\end{gather*}
$$

- If $\mathcal{T}_{s}$ rises, $T_{\mathrm{g}}$ does, too
- If $\mathcal{T}_{t}$ rises, $T_{\mathrm{g}}$ falls
- If $A$ rises, $T_{\mathrm{g}}$ falls
- If adding a greenhouse gas, $\mathrm{d} \mathcal{T}_{s} \gg \mathrm{~d} \mathcal{T}_{t}$, because of spectrum mismatch (visible in, IR out)
- BUT $\mathrm{d} A$ is a complete unknown (clouds, snow, etc.)


## Chapter 2

## Thermodynamics

## Ideal Gas + Hydrostatic $=$ Atmosphere

### 2.1 Check in: : — :, 5 min

- Who has the book?
- Questions?


### 2.2 HW1 Discussion: : - :, 20 min

Props: globe and flashlight

### 2.3 Meaning and Forms of the Ideal Gas Law: : - :, 20 min

- Ideal gas law has 2 pitfalls and several forms
- Pitfall 1: $n$ can be molecules, moles, or implicit; I use $n_{\text {mol }}$ if it's moles
- Pitfall 2: $R=R^{*} / M_{\mathrm{mol}} \neq R^{*} ; R^{*}$ is the universal gas constant
- Form 1: $p V=n_{\text {mol }} R^{*} T —$ good for confined (piston) problems, popular in HS
- Form 2: $p V_{\mathrm{mol}}=R^{*} T$ - chemists like this one. $V_{\mathrm{mol}}=V / n_{\mathrm{mol}}$ is the volume of 1 mole of particles (molar volume, a form of specific volume)
- Form 3: $R_{*}$ is Boltzmann's constant for a mole of gas: $R^{*}=N_{\mathrm{A}} k$
$p V_{\mathrm{mol}}=N_{\mathrm{A}} k T$
$p \frac{n}{N_{\mathrm{A}}} V_{\mathrm{mol}}=n k T$ here $n$ is number of molecules
$p V=n k T$
- Boltzmann's constant relates $T$ to particle energy $[\mathrm{J} / \mathrm{K}]$
- KE on right, what about left?
- $p$ has units of $[F / A]=\left[F / L^{2}\right]$
- $p V$ has units of $[F V / A]=\left[F L^{3} / L^{2}\right]=[F L]=E$
- $p V=n_{\mathrm{mol}} R^{*} T$ (above)
- $p=\frac{n_{\mathrm{mol}} M_{\mathrm{mol}}}{V} \frac{R^{*}}{M_{\mathrm{mol}}} T$
- $\frac{n_{\mathrm{mol}} M_{\mathrm{mol}}}{V}=\rho$
- $p=\rho R T$ - atmospheres:
- Specific gas constant. $R=R^{*} / M_{\mathrm{mol}}$ is gas constant for a gas of molar mass $M_{\mathrm{mol}}$.
- Note that in all of these, $V$ must be small, so $p$ and $T$ do not vary significantly in $V$. Else calculus.
- Sometimes see $\mu$ for molecular mass (also mixing ratio)
- Ideality: Gases are not racist! Partial pressures, partial volumes, mixing ratios, molar masses, etc. all linear in $n_{i}$
- Gases do not contract or expand when mixed at same $T$
- Also, will learn later that $R=c_{p}-c_{v}$ is a form of specific heat.
- When expressed per mole [ $\mathrm{J} / \mathrm{mol} \mathrm{K}$ ], it's universal for all gasses
- When expressed per kg of gas [ $\mathrm{J} / \mathrm{kg} \mathrm{K}$ ] it therefore is not universal
- Both forms have utility in certain problems but have to be converted in others


### 2.4 Isothermal Structure: : — :, 10 min

- Hydrostatic balance

$$
\frac{d p}{d z}=-\rho g
$$



- $g=$ gravity $\left(\mathrm{m} / \mathrm{s}^{2}\right)$
- Area implicit in $p$ (used instead of $f$ )
- Note: $p$ increases downward, $z$ increases up.

Watch integration limits!

- Ideal gas: $\rho=p / R T$
- Assume $T$ constant:

$$
\begin{align*}
\frac{d p}{d z} & =-\rho g  \tag{2.1}\\
\rho & =\frac{M_{\mathrm{mol}} p}{R^{*} T}  \tag{2.2}\\
\frac{d p}{d z} & =-\frac{M_{\mathrm{mol}} g}{R^{*} T} p  \tag{2.3}\\
\frac{d p}{p} & =-\frac{d z}{H}, \quad H=\frac{R^{*} T}{M_{\mathrm{mol}} g}  \tag{2.4}\\
\int_{p_{0}}^{p} \frac{d p^{\prime}}{p^{\prime}} & =-\frac{1}{H} \int_{0}^{z} d z^{\prime}  \tag{2.5}\\
\ln \frac{p}{p_{0}} & =-\frac{z}{H}  \tag{2.6}\\
p(z) & =p_{0} e^{-\frac{z}{H}}  \tag{2.7}\\
\rho(z) & =\rho_{0} e^{-\frac{z}{H}} \tag{2.8}
\end{align*}
$$

- $H=$ scale height $=e$-folding distance for $p$ or $\rho$
- $H=7.6 \mathrm{~km}$ on Earth, 25 km on Jupiter, 55 km on Saturn


### 2.5 Isothermal Examples and Intuition: : - :, 10 min

- Reference geoid: "sea level" on other planets. Mean volumetric ellipsoid, 1-bar level. Different for each planet. Often used for $p_{0}$.
- Mauna Kea is 4200 m above sea level. What is the pressure there?
- In thin atmosphere, what is mass per unit area of air above $p$ ? No integrating! Think of the physical meaning of "pressure."

$$
\begin{align*}
p & =f / A \quad \text { force per unit area }  \tag{2.10}\\
f & =m a  \tag{2.11}\\
a & =g  \tag{2.12}\\
\frac{m}{A} & =\frac{p}{g} \tag{2.13}
\end{align*}
$$

- More intuition:

$$
\begin{align*}
p & =\rho R T  \tag{2.14}\\
& =\rho g H  \tag{2.15}\\
\frac{m}{A} & =\rho H \tag{2.16}
\end{align*}
$$

- Mass of air above you is mass of one scale height of air at your local density. "Turn the atmosphere into an ocean."
- As an astronomer, why would you care about the mass per unit area?



### 2.6 Lapse Rate: : - :, 10 min

- If $T$ not constant...

$$
\begin{array}{rlr}
\int_{p_{0}}^{p} \frac{d p^{\prime}}{p^{\prime}} & =-\frac{M_{\mathrm{mol}} g}{R^{*}} \int_{0}^{z} \frac{d z^{\prime}}{T} \quad T \text { not const. } \\
p(z) & =p_{0} \mathrm{e}^{-\frac{M_{\operatorname{mol}} g}{R^{*}} \int_{0}^{z} \frac{d z^{\prime}}{T\left(z^{\prime}\right)}} \tag{2.18}
\end{array}
$$

- So what can $T$ do? Often it's linear over small ranges
- Lapse rate $\Gamma=-\frac{d T}{d z}=6.5 \mathrm{~K} / \mathrm{km}$ in Earth's troposphere
- Very important!
- Usually $\Gamma>0$ in troposphere, $\Gamma<0$ in stratosphere
- $\Gamma<0$ is an inversion layer: very stable against convection
- Also, if know $p$ and $T$ for two heights, can find $\Delta z$ :
- $g d z=-R T d(\ln p)$
- $z_{2}-z_{1}=-\frac{R}{g} \int_{p_{1}}^{p_{2}} T d(\ln p)$
- OFTEN measure $p, T$ together, e.g., weather balloon, plane
- Find altitude of plane or balloon
- $z_{2}-z_{1}=\frac{R \bar{T}}{g} \ln \left(\frac{p_{1}}{p_{2}}\right) \quad$ watch sign
- Isothermal case is obvious, else define mean $\bar{T}$

$$
\begin{equation*}
\bar{T}=\frac{\int_{p_{2}}^{p_{1}} T d(\ln p)}{\int_{p_{2}}^{p_{1}} d(\ln p)} \tag{2.19}
\end{equation*}
$$

## Potential Temperature

### 2.7 Check in: : — :, 5 min

- http://pds-atmospheres.nmsu.edu/ $\rightarrow$ education $\rightarrow$ encyclopedia
- Who has the book?
- Bring up questions on reading during lecture
- Clarification questions on homework? Due Tuesday.
- Who has done the reading? Remember, weekly assignment is on course schedule, online in handouts directory.
- HW return
- Questions?


### 2.8 Atmospheric Structure: : - :, 15 min

- A thermal profile's independent variable is height or pressure, given on the vertical axis
- The dependent variable is temperature, on the horizontal
- This unusual arrangement physically aligns it with the real atmosphere
- "Spheres" are where $\Gamma=-\mathrm{d} T / \mathrm{d} z$ is positive or negative
- Where it changes sign, have a "pause" of the layer below. E.g., tropopause is at top of troposphere.
- Plots of $T(p)$ are the coin in trade in planetary atmospheres. For the Earth::
- Troposphere: $\frac{d T}{d z}<0$, neutral gas, convection-dominated heat transfer, clouds \& precipitation, weather. $90 \%$ of mass.
- Tropopause: $\frac{d T}{d z}=0$, border between troposphere and stratosphere
- Stratosphere: $\frac{d T}{d z}>0$, mostly neutral, solar photochemistry heats the air locally $\left(\mathrm{O}_{3}\right)$, more at higher levels per unit mass $\Rightarrow$ stably stratified $\Rightarrow$ thin clouds and fast waves. $10 \%$ of mass.
- Stratopause: $\frac{d T}{d z}=0$, border between stratosphere and mesosphere
- Mesosphere: $\frac{d T}{d z}<0$, many ions, species starting to separate, each with its own $H$, thermal IR losses to space dominate solar heating, no $\mathrm{O}_{3} .0 .1 \%$ of mass here and in thermosphere
- Mesopause: $\frac{d T}{d z}=0$, border between mesosphere and thermosphere
- Thermosphere: $\frac{d T}{d z}>0$, breaking vertical gravity waves and solar UV excitation heat the air to extreme temperatures ( $800+\mathrm{K}$ ). Light particles can escape from weaker $g$ fields. Molecules heated and broken up by UV, contains ionosphere
- Clouds: occur at temperatures at or below the condensation and freezing points of a volatile, if there is a large enough supply of the volatile. Clouds imply moving air.
- Exobase: lowest altitude from which molecules can escape to space, in thermosphere
- Exosphere: everything above the exobase, contained in thermosphere
- Homosphere: lower region in which all molecular species are well mixed and follow a single scale height
- Heterosphere: upper region in which species have independent scale heights
- Homopause: altitude border between the homosphere and heterosphere



Source: Wikimedia Commons
http://upload.wikimedia.org/wikipedia/commons/1/18/Atmosphere_with_Ionosphere.svg

### 2.9 Potential Temperature: : - :, $\mathbf{3 0} \mathbf{~ m i n}$

- First law of thermodynamics: $\delta U=\delta Q+\delta W$
- $\delta$ is an "inexact differential", indicating possibility of non-reversible process
- $U$ is internal energy, $Q$ is heat, $W$ is mechanical work, both INto system
- Using state functions (measurable quantities),
- $\delta U=T \delta S-p \delta V$
- Last term negative because decrease in volume is increase in energy.
- $S$ is entropy
- $\delta H=T \delta S+V \delta p$
- $H$ is enthalpy: work extractable at constant pressure
- IF REVERSIBLE:
- $\delta Q=T \delta S$
- $\delta W=-p \delta V$
- For unit mass of ideal gas, $V=1 / \rho$ and
- $U=c_{v} T$
- $c_{v}$ is heat capacity at constant volume, indep of $T$
- $H=c_{v} T+R T=c_{p} T$
- $T \delta S=c_{p} \delta T-\frac{R T}{p} \delta p$
- $\delta S=c_{p} \frac{\delta T}{T}-R \frac{\delta p}{p}=c_{p} \delta(\ln T)-R \delta(\ln p)$
- $S=c_{p} \ln T-R \ln p+\mathrm{const}=c_{p} \ln \left(T p^{-\kappa}\right)+S_{0}$
- $\kappa=R / c_{p}$
- This is all still per unit mass.
- adiabatic: $\delta Q=0$
- Start at $T, p$, move to $\theta, p_{0}$
- If $\delta Q=0$, then $\delta S=0$ (reversible)
- $c_{p} \delta(\ln T)=R \delta(\ln p)$
- Integrate over change:
- $c_{p} \ln \left(\frac{\theta}{T}\right)=R \ln \left(\frac{p_{0}}{p}\right)$
- $\theta=T\left(\frac{p_{0}}{p}\right)^{\kappa}$
- $\theta$, potential temperature, defines "hot air rises".
- Atmosphere is sorted (monotonic) in potential temperature
- $S=c_{p} \ln \theta+S_{1}$
- $\theta$ constant means adiabatic change, and vice versa


## Chapter 3

## Oscillation

### 3.1 Check in: : — :, 0 min

- Point out http://pds-atmospheres.nmsu.edu/ $\rightarrow$ education $\rightarrow$ encyclopedia
- Who has the book?
- Bring up questions on reading during lecture
- Clarification questions on homework? Email jh. Due Tuesday.
- Who has done the reading? Remember, weekly assignment is on course schedule, online in handouts directory.
- Questions?


### 3.2 Adiabatic Lapse Rate: : - :, 25 min

- "Parcel" - same pressure, but maybe different $\rho, T$ or composition as environment
- "Small": does not influence or mix with environment
- In reality, deformation and mixing are efficient w/o containment
- Often considered adiabatic (insulating, thin walls)
- Saw lapse rate, $\Gamma=-\mathrm{d} T / \mathrm{d} z$
- Derive using adiabatic parcel motion
- If adiabatic, $\left(\frac{\mathrm{d} \theta}{\mathrm{d} z}\right)_{\text {parcel }}=0$ and $\left(\frac{\mathrm{d} S}{\mathrm{~d} z}\right)_{\text {parcel }}=0$
- Recall $\delta S=c_{p} \frac{\delta T}{T}-R \frac{\delta p}{p}$
- So $0=\frac{c_{p}}{T}\left(\frac{\mathrm{~d} T}{\mathrm{~d} z}\right)_{\text {parcel }}-\left(\frac{R}{p} \frac{\mathrm{~d} p}{\mathrm{~d} z}\right)_{\text {parcel }}$
- Solve that and use the hydrostatic equation and ideal gas law
$-\left(\frac{\mathrm{d} T}{\mathrm{~d} z}\right)_{\text {parcel }}=-\frac{R T}{c_{p} p}\left(\frac{\mathrm{~d} p}{\mathrm{~d} z}\right)_{\text {parcel }}=\frac{g}{c_{\mathrm{p}}} \equiv \Gamma_{\mathrm{a}}$
- $\Gamma$ is larger under higher $g$, for same gas.
- DRY adiabatic lapse rate $(\mathrm{DALR})=\Gamma_{\mathrm{a}}=9.8 \mathrm{~K} / \mathrm{km}$ on Earth
- Saturated adiabatic lapse rate $(\mathrm{SALR})=3 \mathrm{~K} / \mathrm{km}$ (below freezing) and $4.9 \mathrm{~K} / \mathrm{km}$ (above freezing)
- Actual lapse rate $=\Gamma=6.49 \mathrm{~K} / \mathrm{km}$ (international standard atmosphere, up to $11 \mathrm{~km}=36,090$ $\mathrm{ft})$
- Real $\Gamma$ vs. $\Gamma_{\mathrm{a}}$ determines stability vs. convection.
- If $\Gamma=\Gamma_{\mathrm{a}}, \theta=$ constant, neutral stability.
- If $\Gamma<\Gamma_{\mathrm{a}}$, air above more energetic than below, lofted air falls back, stable.
- If $\Gamma>\Gamma_{\mathrm{a}}$, air above less energetic than below, lofted air rises more! Unstable, convection.
- Air rises at DALR until dew point equals parcel temperature
- Then at SALR (latent heat transfers to air) until air is dry
- Then at DALR



### 3.3 Live Examples: : - :, 15 min

- What are temperature and pressure on Mt. Everest?
- What is $\theta$ on Mt. Everest?


### 3.4 Schedule Presentations: : - :, 10 min

### 3.5 Oscillation and Convection: : - :, 50 min

- FINDME: Draw parcel diagram
- Buoyant force on the parcel $=($ displaced - real mass $) \times g$
- Acceleration? $F=m a$
- $F=g V\left(\rho_{\mathrm{e}}-\rho_{\mathrm{p}}\right)=m a=\rho_{\mathrm{p}} V a$ e denotes the environment, p denotes the parcel.
- $a=g\left(\frac{\rho_{\mathrm{e}}}{\rho_{\mathrm{p}}}-1\right)$
- $\frac{\rho_{1}}{\rho_{2}}=\frac{p_{1}}{R T_{1}} \frac{R T_{2}}{p_{2}}=\frac{T_{2}}{T_{1}}$ because $p_{1}=p_{2}$
- $a=g\left(\frac{T_{\mathrm{p}}}{T_{\mathrm{e}}}-1\right)$
- If, at $p_{0}, T_{\mathrm{p}}=T_{\mathrm{e}}=T_{0}$ :
- $a=g\left(\frac{T_{0}-\Gamma_{a} \delta z}{T_{0}-\Gamma \delta z}-1\right)$
- $a=g\left(\frac{\Gamma-\Gamma_{\mathrm{a}}}{T_{0}-\Gamma \delta z}\right) \delta z=-\frac{g}{T_{0}}\left(\Gamma_{\mathrm{a}}-\Gamma\right) \delta z$
- $\frac{\mathrm{d}^{2} z}{\mathrm{~d} t^{2}}+\frac{g}{T_{0}}\left(\Gamma_{\mathrm{a}}-\Gamma\right) \delta z=0$
- Has form: $\frac{\mathrm{d}^{2} z}{\mathrm{~d} t^{2}}+N^{2} \delta z=0$
- $N^{2}=\frac{g}{T_{0}}\left(\Gamma_{\mathrm{a}}-\Gamma\right)=\frac{g}{T_{0}}\left(\frac{\mathrm{~d} T}{\mathrm{~d} z}+\frac{g}{c_{p}}\right)$
- Brunt-Väisälä (buoyancy) frequency.
- $N^{2}>0$ : simple harmonic motion
- $N^{2}<0$ : growing exponential: rises in height exponentially
- Relate to $\theta$
- $\theta=T\left(\frac{p_{0}}{p}\right)^{\kappa}$
- $\kappa=R / c_{p}$
- Take $\log$ and differentiate with respect to $z$
- $\ln \theta=\ln T+\kappa\left(\ln p_{0}-\ln p\right)$
- $\frac{1}{\theta} \frac{\mathrm{~d} \theta}{\mathrm{~d} z}=\frac{1}{T} \frac{\mathrm{~d} T}{\mathrm{~d} z}-\frac{\kappa}{p} \frac{\mathrm{~d} p}{\mathrm{~d} z}$
- $\frac{1}{\theta} \frac{\mathrm{~d} \theta}{\mathrm{~d} z}=\frac{1}{T} \frac{\mathrm{~d} T}{\mathrm{~d} z}+\frac{\kappa \rho g}{p}$
- $\frac{1}{\theta} \frac{\mathrm{~d} \theta}{\mathrm{~d} z}=\frac{1}{T} \frac{\mathrm{~d} T}{\mathrm{~d} z}+\frac{g}{c_{p} T}$
- $\operatorname{So} N^{2}=\frac{g}{\theta} \frac{\mathrm{~d} \theta}{\mathrm{~d} z}$


### 3.6 Live Example: : - :, 20 min

- What is $N$ at the ground? Break class into groups, use all $3 N$ equations.


### 3.7 Cloud Forms: : - :, 10 min

- Extra credit: photograph/video an atmospheric phenomenon that we don't ordinarily see or notice, understand it, present it. Time-lapse video of buoyant clouds is good. Talk to jh first.
- Appearance of clouds - flat bottom, fluffy vs. flat, anvil
- Smoke pillars and Triton geysers

Energy

### 3.8 Atmospheric Energy: : - :, 10 min

- How much energy in the atmosphere is available to do work, like form and move weather systems?
- Consider potential energy $E_{\mathrm{p}}$
- $E_{\mathrm{p}}$ of a mass element $=\mathrm{d} m g z=(\rho A \mathrm{~d} z) g z$
- $E_{\mathrm{p}}$ of a column is

$$
\begin{align*}
E_{\mathrm{p}} & =\int_{z_{0}}^{\infty} \rho g z \mathrm{~d} z  \tag{3.1}\\
& =-\int_{z_{0}}^{\infty} \frac{\mathrm{d} p}{\mathrm{~d} z} z \mathrm{~d} z \text { hydrostatic }  \tag{3.2}\\
& =\int_{p=0}^{p=p_{0}} z \mathrm{~d} p \text { swapped limits, vars. }  \tag{3.3}\\
& =[z p]_{p=0}^{p=p_{0}}+\int_{z_{0}}^{\infty} p \mathrm{~d} z \text { by parts, swapped } \tag{3.4}
\end{align*}
$$

assuming $z p \rightarrow 0$ and $p \rightarrow 0$ as $z \rightarrow \infty$ (yes, $p$ declining exponential).

$$
\begin{align*}
& =\int_{z_{0}}^{\infty} p \mathrm{~d} z+E_{0}  \tag{3.6}\\
E_{0} & =z_{0} p_{0}
\end{align*}
$$

- Saying $z_{0}$ rather than just $z=0$ accounts for topography
- Now consider internal energy $=c_{v} T$ per unit mass

$$
\begin{equation*}
E_{\mathrm{I}}=\int_{z_{0}}^{\infty} \rho c_{v} T \mathrm{~d} z=\frac{c_{v}}{R} \int_{z_{0}}^{\infty} p \mathrm{~d} z \tag{3.8}
\end{equation*}
$$

- Note same integral!
- Total energy per unit area (i.e., per column) is

$$
\begin{align*}
E_{\mathrm{T}} & =E_{\mathrm{P}}+E_{\mathrm{I}}  \tag{3.9}\\
& =\left(\frac{c_{v}}{R}+1\right) \int_{z_{0}}^{\infty} p \mathrm{~d} z+E_{0}  \tag{3.10}\\
& =\frac{1}{\kappa} \int_{z_{0}}^{\infty} p \mathrm{~d} z+E_{0} \tag{3.11}
\end{align*}
$$

- Integrate this over Earth's surface


### 3.9 Available Potential Energy: : — :, 5 min

- BUT! Can atmosphere's state be moved to 0 PE?
- Not practically, would have to drop to 0 K to reduce height and get energy out.
- How about with adiabatic motions? Lorenz's work.
- For example, tip bottle of separated salad dressing on side.
- Get energy from return of fluid to lower energy state.
- Adiabatic motions are along isentropes (constant- $\theta$ surfaces).
- Consider mass above an isentrope (its height is $z_{1}(x, y)$ ):

$$
\begin{align*}
M_{1} & =\iint_{\text {surface }} \mathrm{d} x \mathrm{~d} y \int_{z_{1}}^{\infty} \rho \mathrm{d} z  \tag{3.12}\\
& =\frac{1}{g} \iint_{\text {surface }} \mathrm{d} x \mathrm{~d} y \int_{0}^{p_{1}} \mathrm{~d} p \text { hydrostatic }  \tag{3.13}\\
& =\frac{1}{g} \iint_{\text {surface }} p_{1}(x, y) \mathrm{d} x \mathrm{~d} y  \tag{3.14}\\
& =\frac{F_{1}}{g} \text { mass above isentrope }  \tag{3.15}\\
& =\frac{1}{g} \iint_{\text {surface }} p_{0}(x, y) \mathrm{d} x \mathrm{~d} y  \tag{3.16}\\
& =\frac{F_{0}}{g} \text { total mass } \tag{3.17}
\end{align*}
$$

- Note: book says $\langle p\rangle$ rather than $F$, but this is wrong.
- Can use to calculate APE.
- Actual APE calculation is hard because 3D data for the entire atmosphere is hard to get (but see problem 2.9 for a simple case).


## Moisture

***** Need to go over this to compare to Jarrad's delivered talk

### 3.10 How Do We Measure Motions?: : - :, 10 min

- When you see a tornado, why is it dark?
- How is the air moving in this room?
- How was the air moving outside this morning?
- What can you tell about air motions at altitude on a clear day?
- How do we measure atmospheric motions on other planets, viewed from afar?
- thin atmosphere ${ }^{\prime}$ and ${ }^{\prime}$ shuttle.jpg
- vortex clouds from• shuttle.jpg
- Jupiter-Earth-Spot comparison.jpg
- Jupiter ${ }^{\circ}$ Cassini.gif
- What's in these pictures? (make list)
- Why can you see these things?


### 3.11 HW 3: : - :, 35 min

Notes below prepared by:
Prof. Csaba Palotai
email: cpalotai@fit.edu

### 3.12 Moisture in the Atmosphere: : - :, 5 min

Water vapor is a minor constituent of Earth's atmosphere. So why do we care about moisture? What are the effects of moisture?

- horizontal transport of heat/moisture/momentum
- vertical transport of heat/moisture/momentum in convective clouds
- modification of the atmospheric and surface radiative fluxes
- latent heat release/consumption from phase changes of water (or other species on other planets)
- modification of the surface hydrology through precipitation



### 3.13 Cloud and Precipitation Formation: : - :, 10 min



### 3.14 How do we quantify moisture?: : - :, 15 min

In a parcel containing a mixture of gases: $n=\sum n_{i}, m=\sum m_{i}$
The ideal gas law $p V=n k T$
Partial pressure and volume: $p_{i}=n_{i} \frac{k T}{V}$ and $V_{i}=n_{i} \frac{k T}{p}$
Vapor pressure, $e$ : the partial pressure exerted by vapor
Specific humidity, $q$ : ratio of vapor to the mass of air.

$$
\begin{equation*}
q_{i}=\frac{m_{i}}{m_{i}+m_{a}}=\frac{\rho_{i}}{\rho} \tag{3.18}
\end{equation*}
$$

Mass mixing ratio, $w$ : ratio of vapor to the mass of dry air.

$$
\begin{equation*}
w_{i}=\frac{\rho_{i}}{\rho_{\mathrm{dry}}}=\frac{R_{m a}}{R_{m w}} \frac{e}{p-e}=\epsilon \frac{e}{p-e} \tag{3.19}
\end{equation*}
$$

$$
\begin{equation*}
\epsilon=m_{w} / m_{a} \tag{3.20}
\end{equation*}
$$

Volume mixing ratio, $v$ : also known as mole fraction.

$$
\begin{gather*}
\hat{v}_{i}=\frac{V_{i}}{V}=\frac{n_{i}}{n}=\frac{e}{p}  \tag{3.21}\\
\hat{v}_{i} \approx \epsilon w_{i} \tag{3.22}
\end{gather*}
$$

Relative humidity, $r$

$$
\begin{equation*}
r=\frac{w_{\mathrm{vap}}}{w_{\mathrm{sat}}}=\frac{w_{\mathrm{vap}}}{\epsilon e_{\mathrm{sat}} / p_{\mathrm{dry}}}, \tag{3.23}
\end{equation*}
$$

Another definition: vapor pressure over the saturation vapor pressure.

$$
\begin{equation*}
r=\frac{e}{e_{\mathrm{sat}}} \approx \frac{w}{w_{\mathrm{sat}}} \approx \frac{q}{q_{\mathrm{sat}}},(e \ll p) \tag{3.24}
\end{equation*}
$$

Equivalent potential temperature, $\theta_{e}$

$$
\begin{equation*}
\theta_{e}=\theta e^{\frac{L w_{e}}{c_{p T}}} \tag{3.25}
\end{equation*}
$$

Solar mole fraction: ratio of number of species atoms to the hydrogen atoms in the Sun. E.g., oxygen 0.00142 , nitrogen 0.000187 , etc.


### 3.15 Phase Changes: : - :, 15 min

Saturation (equilibrium) vapor pressure: the vapor pressure at which phase change occurs at a constant temperature.

$$
\begin{gather*}
L=\int_{h_{1}}^{h_{2}} d h=\int_{u_{1}}^{u_{2}} d u+p_{s} \int_{v_{1}}^{v_{2}} d v=u_{2}-u_{1}+p_{s}\left(v_{2}-v_{1}\right)  \tag{3.26}\\
\frac{d h}{T} \equiv d s \tag{3.27}
\end{gather*}
$$

from (3.26) and (3.27) we get

$$
\begin{equation*}
L=T\left(s_{2}-s_{1}\right)=u_{2}-u_{1}+p_{s}\left(v_{2}-v_{1}\right) \tag{3.28}
\end{equation*}
$$

$$
\begin{equation*}
u_{1}+p_{s} v_{1}-T s_{1}=u_{2}+p_{s} v_{2}-T s_{2} \tag{3.29}
\end{equation*}
$$

This is G , the Gibbs function. It is constant during an isothermal phase change. Let this phase change occur at $T+d T$ and $p_{s}+d p_{s}$, we will have $G+d G$. From the definition of G

$$
\begin{align*}
d G & =d u+p_{s} d v-T d s+v d p_{s}-s d T  \tag{3.30}\\
d G & =v d p_{s}-s d T \tag{3.31}
\end{align*}
$$

Since $d G_{1}=d G_{2}$, we get

$$
\begin{equation*}
v_{1} d p_{s}-s_{1} d T=v_{2} d p_{s}-s_{2} d T \tag{3.32}
\end{equation*}
$$

Let's combine Eqs. 3.28 and a rearranged 3.32 to get the Clausius-Clapeyron equation:

$$
\begin{equation*}
\frac{d p_{s}}{d T}=\frac{L}{T\left(v_{2}-v_{1}\right)} \tag{3.33}
\end{equation*}
$$

Applying it to water vapor under normal atmospheric conditions, assuming vapor as an ideal gas and $v_{2} \gg v_{1}$ :

$$
\begin{equation*}
\frac{d e_{s}}{e_{s}}=\frac{L}{R_{m w}} \frac{d T}{T^{2}} \tag{3.34}
\end{equation*}
$$

Assume L=const. and integrate:

$$
\begin{equation*}
\log _{10} e_{s}=a-\frac{b}{T} \tag{3.35}
\end{equation*}
$$

Deriving similar equations for all phase changes we can construct a phase diagram.



Experimental Data from Dortmund Data Bank. Several Original Sources.


### 3.16 Saturated Adiabatic Lapse Rate (SALR): :- :, 10 min

Consider a parcel of wet air rising adiabatically, until saturated. When lifted further, will the rate of decrease in temperature be less/more/equal than the adiabatic rate? Why?
Using the $1^{\text {st }}$ Law, the equation of state, the hydrostatic equation, and some definitions (for a full derivation of the equation see text) we get

$$
\begin{equation*}
\Gamma_{s}=-\frac{d T}{d z}=\frac{g}{c_{p}}\left(\frac{1+\frac{L}{R_{d}} \frac{w_{s}}{T}}{1+\frac{\epsilon L^{2}}{c_{p} R_{d}} \frac{w_{s}}{T^{2}}}\right) \tag{3.36}
\end{equation*}
$$

### 3.17 Diagrams: : - :, 15 min

It is convenient and useful to represent the vertical profile of the atmosphere on thermodynamic diagrams. An example, the tephigram, is shown in the text (2.9).

Let's define a general expression for $N^{2}$

$$
\begin{equation*}
N^{2}=g^{2}\left[-\rho \beta+\frac{\alpha^{2} T}{c_{p}}+\frac{d \rho_{\text {env }}}{d p}\right] \tag{3.37}
\end{equation*}
$$

Moisture in the atmosphere modifies the $N^{2}$ profile
Average Molar Mass


Skew T-log $p$ diagram and CAPE. Let's introduce the Convective Available Potential Energy (CAPE), it represents the vertically integrated positive buoyancy of a rising parcel and indicates general instability in the atmosphere.

$$
\begin{equation*}
C A P E=\int_{p_{\mathrm{LFC}}}^{p_{\mathrm{LNB}}}\left(v_{\text {parcel }}-v_{\mathrm{env}}\right) d p \tag{3.38}
\end{equation*}
$$

see http://www.tornadochaser.net/cape.html and http://weather.unisys.com/upper ${ }^{\circ}$ air/skew/skew•KJAX.html
***** DOWN TO HERE COMPARING TO ACTUAL LECTURES LAST YEAR
Move this to later:

### 3.18 Presentations: : - :, 45 min

- Please set up during questions for prior speaker
- Give handouts now
- Cutoff at 10 minutes is strict
- Everyone: Take notes both on content and on presentation


## Chapter 4

## Radiation Basics

### 4.1 Check in: : — :, 6 min

- Schedule next topic lectures


### 4.2 Landscape: : - :, 5 min

- 3 ways to move heat: conduction, convection, radiation
- Radiation: energy transmission over distance by photons
- In atmospheres, radiation heats some regions and cools others
- Mixture of macro and quantum physics
- Macro connected to quantum by statistical mechanics
- Processes involved are simple
- Combinations are not, very rich range of behavior
- Encourage exploring with simple calcs of your own, starting from HW5
- E.g., make an emission spectrum, an absorption spectrum, etc. from line lists like HITRAN, or a fake one like HW5's. Then, change the conditions to be like a real atmosphere.
- Show Mars spectrum


### 4.3 Atmospheric Radiation Concepts: : - :, 15 min

- Spectrum = probability distribution of photon energy vs. frequency/wavenumber
- Consider energy to travel as a wave
- Take off and land as a particle
- Sun and Earth are close to blackbodies (atmospheres modify things)
- Earth spectrum is bimodal: reflected sunlight and emitted Earth "thermal" (but both are thermal)
- Also true of all other solar system bodies
- Solar $0.1-4 \mu \mathrm{~m}, 5800 \mathrm{~K}$
- Thermal $4-100 \mu \mathrm{~m}, 288 \mathrm{~K}$
- Radiative transfer studies light absorption and emission
- Photon has energy $E=h \nu$, represents state change $\Delta E$ in atom or molecule
- Spectrum created by thermal (blackbody) and line emission processes
- Spectrum sculpted when passing through gas by line absorption
- Gas passes leave spectral "fingerprints" of composition, $T, P, \rho$
- Multiple passes possible (e.g., though interstellar molecular clouds)
- $E=h \nu=h c / \lambda$ of photon is $\Delta E$ of energy transition in atom or molecule
- Spectroscopic wavenumber $\tilde{\nu}=1 / \lambda$ is NOT $k=2 \pi / \lambda$, the plane-wave wavenumber, see ch 5
- Spectroscopists like $\tilde{\nu}$ because it provides even intervals of energy (10 wavenumbers are the same energy gap no matter where in the spectrum)


### 4.4 Gaining and Losing Photons: : - :, 15 min

- Radiative transfer is computing the gain and loss of photons in a beam
- Must know sources and sinks and their conditions (composition, number density, temperature, etc.)
- Source Processes (emission):
- Bremsstrahlung (e.g., synchrotron radiation) - accelerated charges radiate
* Thermal - collisions accelerate charges, ensemble emission is blackbody
- Line emission
* Atomic energy levels
* Molecular rotation and vibration states
* Ionic (re)combination - either electrons and ions or 2 ions
- Cherenkov radiation - particle moves faster than light in a medium (reactor light)
- Sink processes (extinction):
- Photoexcitation: quantum leap to higher energy level
- Photodissociation: splitting molecules
- Photoionization: ionizing atoms
- Thermalization: collisional transfer to kinetic energy ( $t_{\text {coll }}<t_{\text {emit }}$ )
- Scattering: any re-emission or reflection at same wavelength in (perhaps non-uniform) random direction
- Reflection: coherent scattering (solid surface or droplet)
- Refraction: (solid surface or droplet)
- Rayleigh scattering: continuum scattering by gas molecules
- Mie scattering: continuum scattering by condensate particles


### 4.5 Thermal Radiation: : - :, 20 min

- Blackbody: something that absorbs all light hitting it
- An isothermal cavity is in thermodynamic equillibrium w/ radiation contained in it (inside of a blackbody)
- Blackbody radiation is isotropic
- What do objects in an isothermal cavity look like?
- Planck's function (or law)

$$
\begin{align*}
u_{\nu}(T)=\frac{8 \pi h \nu^{3}}{c^{3}\left(e^{h \nu / k T}-1\right)} & \text { energy density: } \mathrm{J} / \mathrm{m}^{3} / \mathrm{Hz}  \tag{4.1}\\
B_{\nu}(T)=\frac{2 h \nu^{3}}{c^{2}\left(e^{h \nu / k T}-1\right)} & \text { spectral radiance: } \mathrm{W} / \mathrm{m}^{2} / \mathrm{sr} / \mathrm{Hz}  \tag{4.2}\\
B_{\lambda}(T)=\frac{2 h c^{2}}{\lambda^{5}\left(e^{h c / \lambda k T}-1\right)} & \text { spectral radiance: } \mathrm{W} / \mathrm{m}^{2} / \mathrm{sr} / \mu \mathrm{m} \tag{4.3}
\end{align*}
$$

- $h$ has units $[\mathrm{Js}]=[\mathrm{J} / \mathrm{Hz}]$
- Convert $u_{\nu}$ to $B_{\nu}$ considering surface emission into 1 sr cone for time $t$
- 1 sr cone is $1 / 4 \pi$ of total radiation
- Height of cone is $c t$
- $u_{\nu} \cdot c / 4 \pi=B_{\nu}$
- This refers to energy from each point in area $\mathrm{d} A$ within solid angle $\mathrm{d} \Omega$ of a given direction
- Blackbodies emit w/ Planck function
- Planck function curves never intersect

- $\lambda_{\text {max }}=b / T, b=\sim 3 \times 10^{-3} \mathrm{~m} \mathrm{~K}$, Wien's displacement law (where $\frac{\mathrm{d} B_{\lambda}}{\mathrm{d} \lambda}=0$ )
- Peak displaces to shorter $\lambda$ with higher $T$
- Note log behavior on plots, esp. Fig. 3.1, note constant ratio at long $\lambda$, steep dropoff at short end
- Real things emit less $\epsilon_{\nu}=$ spectral emittance
- Real things abosrb less $\alpha_{\nu}=$ spectral absorptance
- Kirchhoff: $\epsilon_{\nu}=\alpha_{\nu}$


### 4.6 Radiometric Quantities: : - :, 15 min

- Most subdisciplines use one or two of these
- Spectral (monochromatic) radiance: $L_{\nu}(\mathbf{r}, \mathbf{s}):\left[\mathrm{W} / \mathrm{m}^{2} / \mathrm{sr} / \mathrm{Hz}\right]$. Power per area per solid angle per unit frequency from point $\mathbf{r}$ in direction $\mathbf{s}$. The basic quantity. $B_{\nu}$ is an example for blackbodies.
- Separate integrals over area and over solid angle in your mind

- Radiance: $L(\mathbf{r}, \mathbf{s})=\int_{0}^{\infty} L_{\nu}(\mathbf{r}, \mathbf{s}) \mathrm{d} \nu\left[\mathrm{W} / \mathrm{m}^{2} / \mathrm{sr}\right]$ frequency
- Irradiance means integrated over 1 hemisphere
- Spectral irradiance: $F_{\nu}(\mathbf{r}, \mathbf{n})=\int_{2 \pi} L_{\nu}(\mathbf{r}, \mathbf{s}) \mathbf{n} \cdot \mathbf{s} \mathrm{d} \Omega(\mathrm{s})\left[\mathrm{W} / \mathrm{m}^{2} / \mathrm{Hz}\right]$ hemisphere
- Irradiance (flux density): $F(\mathbf{r}, \mathbf{n})=\int_{2 \pi} L(\mathbf{r}, \mathbf{s}) \mathbf{n} \cdot \mathbf{s} \mathrm{d} \Omega(\mathrm{s})=\int_{0}^{\infty} F_{\nu}(\mathbf{r}, \mathbf{n}) \mathrm{d} \nu\left[\mathrm{W} / \mathrm{m}^{2}\right]$
- Flux (an irradiance) is parallel (not antiparallel) to a direction
- Net power: $F_{z}=F^{\uparrow}-F^{\downarrow}$


## Chapter 5

## Radiative Transfer Equation

### 5.1 Check in: : — :, 5 min

Spectral radiance
$L_{\nu}(\mathbf{r}, \mathbf{s})$
[W/m²/sr/Hz]
Spectral irradiance
$F_{\nu}(\mathbf{r}, \mathbf{n})=\int_{2 \pi} L_{\nu}(\mathbf{r}, \mathbf{s}) \mathbf{n} \cdot \mathbf{s} \mathrm{d} \Omega(\mathrm{s})$ [W/m²/Hz]

Radiance
$L(\mathbf{r}, \mathbf{s})=\int_{0}^{\infty} L_{\nu}(\mathbf{r}, \mathbf{s}) \mathrm{d} \nu$
[W/m²/sr]
Irradiance (flux density)
$F(\mathbf{r}, \mathbf{n})=\int_{2 \pi} L(\mathbf{r}, \mathbf{s}) \mathbf{n} \cdot \mathbf{s} \mathrm{d} \Omega(\mathrm{s})=\int_{0}^{\infty} F_{\nu}(\mathbf{r}, \mathbf{n}) \mathrm{d} \nu$ [W/m ${ }^{2}$ ]

- Questions?


### 5.2 Local Thermodynamic Equillibrium (LTE): : - :, 5 min

- If matter present in cavity, and collisions not too frequent,
- Then has Boltzmann distribution of states

$$
\begin{equation*}
\frac{n_{1}}{n_{2}}=\frac{g_{1}}{g_{2}} e^{-\Delta E / k T} \tag{5.1}
\end{equation*}
$$

- $g$ is degeneracy, $n$ is number in a given state
- Must have $\tau_{c} \ll \tau_{d}$ to stay in same state
- $\tau_{c}$ is collisional decay time
- $\tau_{d}$ is radiative decay time
- LTE $=$ LOCAL thermodynamic equillibrium
- Lower atmosphere different from upper, change very gradual
- Above $60 \mathrm{~km}(0.1 \mathrm{hPa})$ for rovibrational states
- Above 500 km for translational


### 5.3 Back in Black: : - :, 10 min

- Plane surface at $T$
- $L_{\nu}=B_{\nu}(T)$ is isotropic
- Independent of $\mathbf{s}, \mathbf{r}$, hemispheric integral simplifies
- $F_{\nu}(\mathbf{r}, \mathbf{n})=\int_{2 \pi} L_{\nu} \mathbf{n} \cdot \mathbf{s} \mathrm{d} \Omega(\mathbf{s})=2 \pi B_{\nu} \int_{0}^{\pi / 2} \cos \phi \sin \phi \mathrm{~d} \phi=\pi B_{\nu}(T)$
- $\mathrm{d} \Omega=2 \pi r(\phi) \mathrm{d} \phi=2 \pi \sin \phi \mathrm{~d} \phi$ axisymmetric, $r$ is radius from axis (not center) on unit(less) sphere
- Blackbody radiance: $\int_{0}^{\infty} B_{\nu} \mathrm{d} \nu=\frac{\sigma}{\pi} T^{4}$
- Blackbody irradiance (flux): $F=\sigma T^{4}$ Stefan-Boltzman law


### 5.4 Extinction and Emission: : - :, $\mathbf{3 0} \mathbf{~ m i n}$

- If sinks and sources, then extinction and emission, $L_{\nu}$ changes
- 2 processes separate - never be convinced otherwise!
- Emitted light then undergoes extinction as with initial light
- When traversing distance $\mathrm{d} s$, a fraction $\mathrm{d} L_{\nu} / L_{\nu}$ of photons absorbed
- That fraction proportional to distance and $\rho_{\mathrm{a}}$, dependent on material
- Lambert's law: $\mathrm{d} L_{\nu}=-k_{\nu}(s) \rho_{\mathrm{a}}(s) L_{\nu} \mathrm{d} s$
- Extinction coefficient $k_{\nu}=a_{\nu}+s_{\nu}$ (absorption and scattering coefficients)
- $\rho_{\mathrm{a}} \neq \rho$, rather just the partial density of (each) active absorber
- If emitting, add term for that, proportional to mass $\rho_{\mathrm{a}} \mathrm{d} s$
- Convenient to write $k_{\nu}(s) \rho_{\mathrm{a}}(s) J_{\nu} \mathrm{d} s$
- $J_{\nu}$ is the source function
- Radiative-transfer equation (Schwarzschild eq.): $\frac{\mathrm{d} L_{\nu}}{\mathrm{d} s}=-k_{\nu}(s) \rho_{\mathrm{a}}(s)\left(L_{\nu}-J_{\nu}\right)$
- $k_{\nu}, \rho_{\mathrm{a}}, J_{\nu}$, and $L_{\nu}$ can vary with location $s$ along beam
- Define optical depth or optical path or optical thickness proportional to total mass (acts as distance variable):
$\tau_{\nu}(s)=\int_{s_{0}}^{s} k_{\nu}\left(s^{\prime}\right) \rho_{\mathrm{a}}\left(s^{\prime}\right) \mathrm{d} s^{\prime}$
Note: Usually optical depth is $\tau$, but our book uses that for something else.
- Then: $\frac{\mathrm{d} L_{\nu}}{\mathrm{d} \tau_{\nu}}+L_{\nu}=J_{\nu}$
- Multiply by $e^{\tau_{\nu}}$, integrate
- $L_{\nu} e^{\tau_{\nu}}=\int J_{\nu} e^{\tau_{\nu}^{\prime}} \mathrm{d} \tau_{\nu}^{\prime}+C$
- Call beam $L_{\nu 0}$ at $s=0$
- Then $L_{\nu}(s)=\int_{0}^{\tau_{\nu}} J_{\nu}\left(\tau^{\prime}\right) e^{-\left(\tau_{\nu}-\tau^{\prime}\right)} \mathrm{d} \tau^{\prime}+L_{\nu 0} e^{-\tau_{\nu}}$
- Integrate emission from each point in beam, attenuate from there to location $\tau_{\nu}$
- Add original radiation, attenuated over full beam
- If $J_{\nu}=0$, beam falls exponentially (Beer's law:

The taller the glass,
The darker the brew,
The dimmer the light
That makes it through.)

- "Optically thick" = hard to see through, $\tau_{\nu} \geq 1$
- "Optically thin" $=$ easy to see through, $\tau_{\nu} \leq 1$
- Example:
- $k_{\nu}, \rho_{\mathrm{a}}$ constant, $s_{0}=0$, then:
- $L_{\nu}(s)=k_{\nu} \rho_{\mathrm{a}} \int_{0}^{s} J_{\nu}\left(s^{\prime}\right) e^{-k_{\nu} \rho_{\mathrm{a}}\left(s-s^{\prime}\right)} \mathrm{d} s^{\prime}+L_{\nu 0} e^{-k_{\nu} \rho_{\mathrm{a}} s}$


### 5.5 Student Report: : - :, 25 min

### 5.6 HW4 Discussion: : - :, 45 min

## Chapter 6

## Spectral Line Formation

### 6.1 Check in: : — :, 5 min

- What are the units on $k_{\nu}$ ?


### 6.2 Planck as Source Function: : - :, 5 min

- What is source function? W/o scattering, at LTE, it's $B_{\nu}$ !
- Under LTE, Kirchhoff's law says $\epsilon_{\nu}=\alpha_{\nu}$
- Emission from $\rho_{a} \mathrm{~d} s$ is $k_{\nu} \rho_{a} \mathrm{~d} s J_{\nu}$
- Absorption is $k_{\nu} \rho_{a} \mathrm{~d} s L_{\nu}$
- $\epsilon_{\nu}=k_{\nu} \rho_{a} \mathrm{~d} s J_{\nu} / B_{\nu}$
- $\alpha_{\nu}=k_{\nu} \rho_{a} \mathrm{~d} s L_{\nu} / L_{\nu}=k_{\nu} \rho_{a} \mathrm{~d} s$ (no scattering)
- But, $\epsilon_{\nu}=\alpha_{\nu}$
- So $J_{\nu}=B_{\nu}$


### 6.3 Diffuse Approximation: : - :, 10 min

- Often assume only vertical matters
- Things depend only on $z$
- Plane-parallel atmosphere approximation
- Avoid integrating over $\Omega$ (complicated)
- Consider random paths
- Then $\tau_{\nu}^{*}=1.66 \tau_{\nu}$, typical path length
- This is the diffuse approximation $\frac{\mathrm{d} F_{\nu}^{\downarrow}}{\mathrm{d} \tau_{\nu}^{*}}+F_{\nu}^{\downarrow}=\pi B_{\nu}$
- No clouds. Works best for upper atmosphere.
- Similar equation holds for upward flux


### 6.4 Molecular Quantum States: : - :, 15 min

- QM says certain states of small things have discrete values
- Electronic excitation states (atoms)
- Vibration (molecules)
- Rotation (molecules)
- Each has associated energy and degeneracy (selection)
- Compare:

| Type of state | $\Delta E$ in... | $\Delta E$ | Degeneracy |
| ---: | :--- | :---: | :---: |
| Electronic excitation | UV/Optical | $-h c R_{\infty} \frac{Z^{2}}{n^{2}}$ | $2 n^{2}$ |
| Vibration (molecules) | Near IR | $h \nu_{0}\left(v+\frac{1}{2}\right)$ | $1+$ |
| Rotation (molecules) | Submillimeter | $\frac{\hbar^{2}}{2 I} J(J+1)$ | $2 J+1$ |

- Electronic and rotational states are familiar
- Vibration states numerous, named
- Can dissociate atom in higher $E$ states
- Atoms have few dozen states, dozens - 1000s of transitions
- Molecules have 1000 s of states, $\sim 1 \mathrm{e} 9$ transitions for $\mathrm{H}_{2} \mathrm{O}$ !
- Massive line databases exist


## Chapter 7

## Spectral Line Shapes

### 7.1 Check in: : — :, 5 min

- Talk schedule


### 7.2 Line Shapes: : - :, $5 \mathbf{m i n}$

- Ideally, $k_{\nu}=\sum_{n} S_{n} \delta\left(\nu-\nu_{n}\right)$, where $S_{n}$ is line strength
- Really, physics happen
- $k_{\nu}=\sum_{n} S_{n} f_{n}\left(\nu-\nu_{n}\right)$
- $f_{n}$ is line shape function, $1=\int_{-\infty}^{\infty} f_{n}\left(\nu-\nu_{n}\right) \mathrm{d} \nu$
- $f_{\nu}$ looks vaguely Gaussian, with "wings" that can be very broad, centered on $\nu_{n}$
- Width and exact shape determined by several factors


### 7.3 Collisional (Natural) Broadening: : - :, 20 min

- Particle collision interval $\tau_{\mathrm{c}}$
- State natural lifetime $\tau_{\mathrm{n}}$
- Heisenberg: $\Delta t \Delta E \geq \hbar / 2$
- $\Delta E=\hbar / \tau$ spread of energies about $E$
- Lorentz line shape: $f\left(\nu-\nu_{n}\right)=\left(\frac{\gamma_{\mathrm{L}}}{\pi}\right) \frac{1}{\left(\nu-\nu_{n}\right)^{2}+\gamma_{\mathrm{L}}^{2}}$
- $\gamma_{\mathrm{L}}=1 /\left(2 \pi \tau_{\mathrm{c}}\right)$ is half-width at half-maximum
- Get $\tau_{\mathrm{c}}$ from kinetic theory, $v \propto(k T)^{1 / 2}$ from kinetic theory, number density $\propto p / T$, collision cross-section
- $\gamma_{\mathrm{L}} \propto p T^{-1 / 2}$
- Similar for natural broadening
- Usually $\tau_{\mathrm{c}}<\tau_{\mathrm{n}}$, except for electronic transitions (UV)
- High-pressure gas has broader lines than low-pressure
- Looks more triangular than Gaussian


### 7.4 Doppler Broadening: : - : 15 min

- Gas particles move, and moving emission is Doppler-shifted
- Random motion of particles in a gas broadens lines
- If $u \ll c, u$ is velocity away:
- Doppler shift: $\nu=(1-u / c) \nu_{0}$
- Note sign correction to book equation, p. 68
- So $u=c\left(\nu_{0}-\nu\right) / \nu_{0}$
- And $\mathrm{d} u / \mathrm{d} \nu=-c / \nu_{0}$
- Gas has a Maxwell-Boltzmann velocity distribution:

$$
P(u)=\sqrt{\frac{m}{2 \pi k T}} e^{-\frac{m u^{2}}{2 k T}}
$$

- This is probability for velocity in $(u, u+\mathrm{d} u$ ]
- (Capital $P$ to distinguish from pressure)
- Just a Gaussian centered on 0 - not speed or energy distribution
- $P(\nu)=P(u)|\mathrm{d} u / \mathrm{d} \nu|$ from probability
- $P(\nu)=c / \nu_{0} \sqrt{\frac{m}{2 \pi k T}} e^{-\frac{m\left[c\left(\nu_{0}-\nu\right) / \nu_{0}\right]^{2}}{2 k T}}=\sqrt{\frac{m c^{2}}{2 \pi k T \nu_{0}^{2}}} e^{-\frac{m c^{2}\left(\nu_{0}-\nu\right)^{2}}{2 k T \nu_{0}^{2}}}=\frac{1}{\sqrt{\pi \gamma_{\mathrm{D}}^{2}}} e^{-\frac{\left(\nu-\nu_{0}\right)^{2}}{\gamma_{\mathrm{D}}^{2}}}$
- $\gamma_{\mathrm{D}}=\frac{\nu_{0}}{c}\left(\frac{2 k T}{m}\right)^{1 / 2}$
- Gaussian width: $\gamma_{\mathrm{D}} \sqrt{2}$
- $k_{\nu}=S P(\nu), S$ is line strength
- $\gamma_{\mathrm{D}} \propto T^{1 / 2}$, independent of $p$
- Voigt line shape combines (convolves) Doppler, collisional, and natural line shapes - not analytic (image)
- $p$ dependence makes collisional dominate in lower atm, Doppler higher ( $>30 \mathrm{~km}$ )
- All planets have a stratosphere no deeper than where collisional broadening starts to become important.
- There, the many, narrow, individual spectral lines broaden enough to merge, and there is opacity at all wavelengths.



### 7.5 Transmittance, Bands, Blending: : - :, 25 min

- Always measure in channels - filter or spectrograph
- Convolve instrument resolution element (based on slit width in $\nu$ space) with real spectrum
- Lines overlap (blend)
- In absorption, lines saturate
- In absorption, care about fraction of energy that gets through, for heating and spectroscopy
- Can't sum line areas to get fraction transmitted
- Transmittance or transmission function $\mathcal{T}_{\nu}=e^{\left(-\left|s_{s_{1}}^{s_{2}} k_{\nu}(s) \rho(s) \mathrm{d} s\right|\right)}=e^{-\left|\tau_{\nu}\left(s_{2}\right)-\tau_{\nu}\left(s_{1}\right)\right|}$
- $p, T$ fixed:
- $\mathcal{T}_{\nu}=e^{-k_{\nu}(p, T) u_{\mathrm{a}}\left(s_{1}, s_{2}\right)}$
- $u_{\mathrm{a}}=\int_{s_{1}}^{s_{2}} \rho_{\mathrm{a}}(s) \mathrm{d} s$
- This is mass of absorber per cross-sectional area
- If $\rho_{\mathrm{a}}$ constant, $u_{\mathrm{a}}=\rho_{\mathrm{a}} l, l$ is path length
- Band transmittance or filter transmission $\overline{\mathcal{T}}_{\mathrm{r}}=\frac{1}{\Delta \nu_{\mathrm{r}}} \int_{\Delta \nu_{\mathrm{r}}} \mathcal{T}_{\nu} \mathrm{d} \nu$
- Band absorptance is $\overline{\mathcal{A}}_{\mathrm{r}}=1-\overline{\mathcal{T}}_{\mathrm{r}}$
- Equivalent width is a way of measuring band strength:
$\mathcal{W}_{\mathrm{r}}=\int_{\Delta \nu_{\mathrm{r}}}\left(1-\mathcal{T}_{\nu}\right) \mathrm{d} \nu=\Delta \nu_{\mathrm{r}}\left(1-\overline{\mathcal{T}}_{\mathrm{r}}\right)=\Delta \nu_{\mathrm{r}} \overline{\mathcal{A}}_{\mathrm{r}}$
- If you have one line, its equivalent width is the width of a box of complete absorption with equal area to the line


### 7.6 1D Atmospheric Radiative Transfer - Setup: : - :, min

- Consider a column of atmosphere (Draw)
- It has a thermal profile, $T(p)$ (Draw)
- It has profiles of chemical abundances, $A_{i}(p)=p_{i}(p) / p$ (Draw)
- The changing pressure makes line widths change with altitude
- How do they change?
- What effect does this have between line peaks?
- What function does the relative abundance of a well-mixed species follow?
- Recall Kirchoff's laws of radiation
- How does the temperature affect the spectrum?
- If the gas is cooler above than below, what do you see?
- If the gas is warmer above than below, what do you see?
- What is the spectrum of an optically thick, well mixed gas?
- Contribution function


### 7.7 Spectra of Some Key Gases: : — :, 10 min

- $\mathrm{CH}_{4}$
- $\mathrm{CO}_{2}$
- CO
- $\mathrm{H}_{2} \mathrm{O}$
- $\mathrm{NH}_{3}$
- Lines at high spectral resolution


### 7.8 3D Atmospheric Spectra: : - :, 10 min

- Path length $v s$. emission angle
- Effect on profiles and contribution function
- Summing the spectra
- Physically inconsistent spectra possible


### 7.9 Transmission and Emission Observations: : - :, min


https://qph.fs.quoracdn.net/main-qimg-b81fd129b1f4a7e7cc2ce132c8dd5ae1-c
7.10 Retrieval: : — :, 15 min

## Chapter 8

## Atmospheric Dynamics

Thanks to Csaba Palotai for preparing and sharing the notes on Atmospheric Dynamics.

### 8.1 Material Derivative: : - :, $\mathbf{1 5} \mathbf{m i n}$

- Consider a fluid element enclosing the same atoms at all times as the fluid moves
- It has a property $A$ (e.g., temperature, density, velocity component, etc.):

$$
A=A(t, x, y, z)=A(\mathbf{r}, t)
$$

- This element is at $(x(t), y(t), z(t))$
- It moves from $(\mathrm{x}, \mathrm{y}, \mathrm{z})$ to $(x+\delta x, y+\delta y, z+\delta z)$ in time $\delta t$
- This results in a change $\delta A$ :

$$
\delta A=\frac{\partial A}{\partial t} \delta t+\frac{\partial A}{\partial x} \delta x+\frac{\partial A}{\partial y} \delta y+\frac{\partial A}{\partial z} \delta z .
$$

- Now, divide by $\delta t$ and let $\delta t=>d t$
- The observed rate of change of A for the fluid element is then

$$
\frac{d A}{d t}=\frac{\partial A}{\partial t}+\frac{\partial A}{\partial x} \frac{d x}{d t}+\frac{\partial A}{\partial y} \frac{d y}{d t}+\frac{\partial A}{\partial z} \frac{d z}{d t}
$$

- The velocity of the fluid element is:

$$
\frac{d \mathbf{r}}{d t}=\mathbf{u}=[u, v, w]=\left[\frac{d x}{d t}, \frac{d y}{d t}, \frac{d z}{d t}\right]
$$

- Thus,

$$
\frac{d A}{d t}=\frac{\partial A}{\partial t}+u \frac{\partial A}{\partial x}+v \frac{\partial A}{\partial y}+w \frac{\partial A}{\partial z}=\frac{\partial A}{\partial t}+\mathbf{u} \cdot \nabla A
$$

- In fluid dynamics, we denote this rate of change by $D / D t$, the material derivative, which is a differential operator

$$
\frac{D}{D t} \equiv \frac{\partial}{\partial t}+\mathbf{u} \cdot \nabla
$$

### 8.2 Conservation of Mass, Continuity Equation: : - :, 20 min

- Consider a fluid element of volume $V$
- Surrounded by a surface $S$
- $A$ is a physical property per unit volume (density, energy, etc.)
- $\sigma[A]$ is the source term (production rate) of $A$ in the volume. (What could some examples be?)
- $\mathbf{F}$ is the flux of $A$
- $\mathbf{F}_{n}$ is $\mathbf{F}$ 's components normal to $S$
- According to the conservation law,

$$
\frac{d}{d t} \int_{V} A d V=-\int_{S} \mathbf{F}_{n} d S+\int_{V} \sigma[A] d V
$$

- Substituting Gauss' Law,

$$
\int_{S} \mathbf{F}_{n} d S=\int_{V} \nabla \cdot \mathbf{F} d V
$$

we get

$$
\frac{d}{d t} \int_{V} A d V=-\int_{V} \nabla \cdot \mathbf{F} d V+\int_{V} \sigma[A] d V
$$

- By the Leibnitz Integral Rule (see simple proof on Wikipedia),

$$
\frac{\mathrm{d}}{\mathrm{~d} t}\left(\int_{V} f(t, V) \mathrm{d} V\right)=\int_{V} \frac{\partial}{\partial t} f(t, V) \mathrm{d} V
$$

- Substituting $\mathbf{F}=A \mathbf{u}$ and differentiating $d V$, we get

$$
\frac{\partial}{\partial t} A+\nabla \cdot(A \mathbf{u})=\sigma[A]
$$

- Consider density, with conservation of mass.
- If we set the source term to zero, we get

$$
\frac{\partial \rho}{\partial t}+\nabla \cdot(\rho \mathbf{u})=0
$$

Expanding $\nabla \cdot(\rho \mathbf{u})$ we get

$$
\begin{gathered}
\frac{\partial \rho}{\partial t}+\mathbf{u} \cdot \nabla \rho+\rho \nabla \cdot \mathbf{u}=0 \\
\frac{D \rho}{D t}+\rho \nabla \cdot \mathbf{u}=0
\end{gathered}
$$

### 8.3 Conservation of Momentum: Navier-Stokes Equation: : :, 20 min

- Apply Newton's Second Law to a small, moving fluid element
- Account for forces
- Pressure gradient force on fluid element:

$$
F_{p, x}=p d y d z-\left(p+\frac{\partial p}{\partial x} d x\right) d y d z=-\frac{\partial p}{\partial x} d x d y d z
$$

- Divide by the mass of the element, $(\rho d x d y d z)$, the net force per unit mass (acceleration) in the $x$ direction is $-(1 / \rho)(\partial p / \partial x)$. The three-dimensional pressure force is

$$
\mathbf{F}_{p}=-\frac{1}{\rho} \nabla p=-\frac{1}{\rho}\left(\mathbf{i} \frac{\partial p}{\partial x}+\mathbf{j} \frac{\partial p}{\partial y}+\mathbf{k} \frac{\partial p}{\partial z}\right)
$$

- The gravitational force is $\mathbf{F}_{g}=-g \mathbf{k}$. (Note: $\mathbf{g}=\nabla \mathbf{\Phi}$ )
- The net frictional (viscous) force acting on the fluid element in the $x$ direction is

$$
F_{v, x}=\left(\tau_{x}+\frac{\partial \tau_{x}}{\partial z} \delta z\right) \delta x \delta y-\tau_{x} \delta x \delta y
$$

- Substituting $\tau=\mu \partial u / \partial z$ and dividing by the mass of the element, we get the net force per unit mass:

$$
F_{v, x}=\frac{1}{\rho} \frac{\partial \tau_{x}}{\partial z}=\frac{1}{\rho} \frac{\partial}{\partial z}\left(\mu \frac{\partial u}{\partial z}\right)=\frac{\mu}{\rho} \frac{\partial^{2} u}{\partial z^{2}} \Rightarrow \mathbf{F}_{v}=\frac{\mu}{\rho} \nabla^{2} \mathbf{u}
$$

- Note: In the book the dynamic viscosity coefficient is $\eta$.
- Note2: $+\frac{1}{3} \nabla(\nabla \cdot \mathbf{u})$ appears in the book, but we can't find it in other books. Perhaps it is small and usually ignored.
- Putting the components together we get the Navier-Stokes equation:

$$
\frac{D \mathbf{u}}{D t}=-\frac{1}{\rho} \nabla p-g \mathbf{k}+\frac{\mu}{\rho} \nabla^{2} \mathbf{u}
$$

- We ignored magnetic forces, which can be important in ionized atmospheres like the sun, hot Jupiters, aurorae, comet tails, etc.


### 8.4 Rotating Frames of Reference: : - :, 20 min

If the angular velocity of the rotating frame is $\Omega$, then the time derivative of a vector $\mathbf{A}$ can be written as

$$
\left(\frac{d \mathbf{A}}{d t}\right)_{i}=\left(\frac{d \mathbf{A}}{d t}\right)_{r}+\boldsymbol{\Omega} \times \mathbf{A}
$$

e.g., substituting the position vector $\mathbf{r}$ we get $\mathbf{u}_{i}=\mathbf{u}_{r}+\boldsymbol{\Omega} \times \mathbf{r}$. If we substitute $\mathbf{u}_{i}$ we get

$$
\left(\frac{d \mathbf{u}_{i}}{d t}\right)_{i}=\left(\frac{d \mathbf{u}_{r}}{d t}\right)_{r}+2 \boldsymbol{\Omega} \times \mathbf{u}_{r}+\boldsymbol{\Omega} \times(\boldsymbol{\Omega} \times \mathbf{r}),
$$

where $-2 \boldsymbol{\Omega} \times \mathbf{u}_{r}$ is the Coriolis force and $-\boldsymbol{\Omega} \times(\boldsymbol{\Omega} \times \mathbf{r})$ is the centrifugal force. Using the expression above we can write the momentum equation in a rotating frame as

$$
\frac{D \mathbf{u}_{r}}{D t}=-\frac{1}{\rho} \nabla p-2 \boldsymbol{\Omega} \times \mathbf{u}_{r}-\boldsymbol{\Omega} \times(\boldsymbol{\Omega} \times \mathbf{r})-g \mathbf{k}+\frac{\mu}{\rho} \nabla^{2} \mathbf{u}_{r}
$$

### 8.5 Energy Equation: : - :, 20 min

The 1st Law:

$$
T d s=d u+p d v=c_{v} d T+p d v
$$

Note: $\alpha$ is often used for specific volume.
Differentiating the gas law WRT time we get

$$
p \frac{d v}{d t}+v \frac{d p}{d t}=R \frac{d T}{d t}
$$

Combining the two equations and using $c_{p}+c_{v}=R$

$$
T d s=c_{p} d T-\frac{1}{\rho} d p
$$

and in Lagrangian form

$$
\dot{Q} \equiv T \frac{D s}{D t}=c_{p} \frac{D T}{D t}-\frac{1}{\rho} \frac{D p}{D t}
$$

$\dot{Q}$ : diabatic heating rate per unit mass. What kind of processes can contribute to $\dot{Q}$ ? If $\dot{Q}=0$ then

$$
\frac{D T}{D t}=\frac{1}{c_{p} \rho} \frac{D p}{D t}
$$

Adiabatic motion means constant potential temperature. It is convenient to write the energy equation in terms of $\theta$

$$
\frac{D \theta}{D t}=\frac{\dot{Q}}{c_{p}}\left(\frac{p}{p_{0}}\right)^{-\kappa}
$$

### 8.6 Governing Equation Summary: : - :, 20 min

$$
\begin{gathered}
\frac{D \rho}{D t}+\rho \nabla \cdot \mathbf{u}_{r}=0 \\
\frac{D \mathbf{u}_{r}}{D t}=-\frac{1}{\rho} \nabla p-2 \cdot \boldsymbol{\Omega} \times \mathbf{u}_{r}-\boldsymbol{\Omega} \times(\boldsymbol{\Omega} \times \mathbf{r})-g \mathbf{k}+\frac{\eta}{\rho} \nabla^{2} \mathbf{u}_{r} \\
T \frac{D s}{D t}=c_{p} \frac{D T}{D t}-\frac{1}{\rho} \frac{D p}{D t}
\end{gathered}
$$

How many unknowns and how many equations?

### 8.7 Spherical Coordinates: : - :, 10 min



Credit: William H. Brune, Penn State College of Earth and Mineral Sciences.
The natural coordinates are the spherical coordinates $(r, \phi, \lambda)$. The distance components $(x, y, z)$ and the velocity components $(u, v, w)$ follow the unit vectors $(\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}})$, respectively. We can introduce small increment distances

$$
\begin{aligned}
d x & =r \cos \phi d \lambda \\
d y & =r d \phi \\
d z & =d r
\end{aligned}
$$

in the zonal, meridional, vertical direction (note: $r=a+z=>d r=d z$. $a$ is the planet's radius).

Starting with the Navier-Stokes equation, ignoring viscosity, and working per unit mass (so force equals acceleration),

$$
\begin{aligned}
-\frac{1}{\rho} \nabla p-g \mathbf{k}+\frac{\mu}{\rho} \nabla^{2} \mathbf{u} & =\frac{D \mathbf{u}}{D t} \\
\frac{D u}{D t}-\left(2 \Omega+\frac{u}{r \cos \phi}\right)(v \sin \phi-w \cos \phi)+\frac{1}{\rho} \frac{\partial p}{\partial x} & =F^{x} \\
\frac{D v}{D t}+\frac{w v}{r}+\left(2 \Omega+\frac{u}{r \cos \phi}\right)(u \sin \phi)+\frac{1}{\rho} \frac{\partial p}{\partial y} & =F^{y} \\
\frac{D w}{D t}-\frac{u^{2}+v^{2}}{r}-2 \Omega u \cos \phi+\frac{1}{\rho} \frac{\partial p}{\partial z}+g & =F^{z}
\end{aligned}
$$

### 8.8 Approximations to the Spherical Equations: : - :, 10 min

Let's introduce

$$
\begin{aligned}
f & =2 \Omega \sin \phi \\
f_{*} & =2 \Omega \cos \phi
\end{aligned}
$$

the Coriolis parameter and the reciprocal Coriolis parameter, respectively.
When investigating small regions, we can introduce a tangent plane with Cartesian coordinates and we can replace $f(\phi)$ with $f_{0}=2 \Omega \sin \phi_{0}=$ const. This is called $\mathbf{f}$-plane approximation. When we investigate a larger region using the tangent-plane approximation but want to consider some variation of $f$, we can use a Taylor expansion of $f(\phi)$ about $\phi=\phi_{0}$

$$
f(\phi)=2 \Omega \sin \phi=2 \Omega\left[\sin \phi_{0}+\left(\phi-\phi_{0}\right) \cos \phi_{0}+\ldots\right]
$$

on the tangent plane. Using $\phi-\phi_{0} \approx y / a$ (a: the planet's radius, y : distance from the center latitude of the plane in the $y$-direction), we get $f(y) \approx f_{0}+\beta y$, where $\beta=\frac{2 \Omega \cos \phi_{0}}{a}=\left(\frac{d f}{d y}\right)_{y=0}$. This is the $\beta$-plane approximation.

### 8.9 Scale Analysis: : - :, 10 min

We can simplify the governing equations by doing scale analysis on the terms and eliminating the negligible ones. E.g., let's simplify the vertical momentum equation, it reduces to hydrostatic balance.

| Scale | Symbol | Typical Magnitude |
| :--- | :---: | :---: |
| Horizontal Scale | $L$ | $1000 \mathrm{~km}=10^{6} \mathrm{~m}$ |
| Vertical Scale | $H$ | $10 \mathrm{~km}=10^{4} \mathrm{~m}$ |
| Horizontal Velocity | $U$ | $10 \mathrm{~m} / \mathrm{s}$ |
| Vertical velocity | $W$ | $10^{-2} \mathrm{~m} / \mathrm{s}$ |
| Timescale | $T$ | 1 day $\sim 10^{5} \mathrm{~s}$ |
| Surface density | $\rho$ | $1 \mathrm{~kg} / \mathrm{m}^{3}$ |
| Earth's radius | $a$ | $6.4 \times 10^{6} \mathrm{~m}$ |
| $2 \times$ rotation rate | $2 \Omega$ | $10^{-4} \mathrm{rad} / \mathrm{s}$ |
| Acceleration of gravity | $g$ | $10 \mathrm{~m} / \mathrm{s}$ |

To analyze our equations and/or to validate certain simplifications we can form dimensional (e.g., $\partial u / \partial t=>U / T$ ) and dimensionless numbers (e.g., $R o=U / \Omega L$ ) that help us to determine the nature of the flow.

Assuming we're not at the poles $(\cos \phi \rightarrow 0)$, vertical velocities are much less than horizontal velocities, and vertical friction to be zero, the momentum equations can be written as

$$
\begin{aligned}
\frac{D u}{D t}-f v+\frac{1}{\rho} \frac{\partial p}{\partial x} & =F^{x} \\
\frac{D v}{D t}+f u+\frac{1}{\rho} \frac{\partial p}{\partial y} & =F^{y} \\
\frac{D w}{D t}+\frac{1}{\rho} \frac{\partial p}{\partial z}+g & =0
\end{aligned}
$$

Expanding the left hand side of the vertical momentum equation we get

$$
\frac{D w}{D t}=\frac{\partial w}{\partial t}+u \frac{\partial w}{\partial x}+v \frac{\partial w}{\partial y}+w \frac{\partial w}{\partial z}
$$

We can estimate the order of each terms

$$
\frac{W}{T} \sim 10^{-7} \mathrm{~m} \mathrm{~s}^{2}, \frac{U W}{L} \sim 10^{-7} \mathrm{~m} \mathrm{~s}^{2}, \frac{W^{2}}{H} \sim 10^{-8} \mathrm{~m} \mathrm{~s}^{2}
$$

but, $g \sim 10^{1} \mathrm{~m} \mathrm{~s}^{2}$. Thus, the pressure term has to balance the gravity term $=>$. The equation reduces to hydrostatic balance.

### 8.10 Geostrophic Flow: : - :, 10 min

We can do a scale analysis on the horizontal momentum equation, too.

$$
\begin{gathered}
\frac{\partial u}{\partial t} \sim \frac{U}{T} \sim 10^{-4} m s^{2}, u \frac{\partial u}{\partial x} \sim \frac{U^{2}}{L} \sim 10^{-4} \mathrm{~m} s^{2}, w \frac{\partial u}{\partial z} \sim \frac{W U}{H} \sim 10^{-5} \mathrm{~ms}^{2} \\
f v=2 \Omega v \sin \phi \sim 2 \Omega U \sim 10^{-3} \mathrm{~ms}^{2}
\end{gathered}
$$

The term $f v$ has to be in balance with the pressure term, thus

$$
f v=\frac{1}{\rho} \frac{\partial p}{\partial x} ; f u=-\frac{1}{\rho} \frac{\partial p}{\partial y}
$$

What does this mean, why is this important? Geostrophic wind blows parallel to the isobars with low pressure on the left (on the northern Hemisphere).
Note: these equations are valid only under certain conditions.
Note2: at low latitudes $f$ is small and it's difficult to establish this balance.

### 8.11 Thermal Wind Equations: : - :, 10 min

Let's analyze the geostrophic equations and the hydrostatic equation. It can be shown that the vertical shear of the geostrophic wind is related to the horizontal temperature gradient.

$$
f v=\frac{1}{\rho} \frac{\partial p}{\partial x} ; f u=-\frac{1}{\rho} \frac{\partial p}{\partial y} ; g=-\frac{1}{\rho} \frac{\partial p}{\partial z}
$$

We can eliminate $\rho$ from the equations using the equation of state

$$
\frac{f v}{T}=R \frac{\partial \ln p}{\partial x} ; \frac{f u}{T}=-R \frac{\partial \ln p}{\partial y} ; \frac{g}{T}=-R \frac{\partial \ln p}{\partial z}
$$

We're cross-differenciating between the first and third, and then the second and third equations to eliminate pressure, and we get

$$
\frac{\partial}{\partial z}\left(\frac{f v}{T}\right)=-\frac{\partial}{\partial x}\left(\frac{g}{T}\right) ; \frac{\partial}{\partial z}\left(\frac{f u}{T}\right)=\frac{\partial}{\partial y}\left(\frac{g}{T}\right)
$$

after completing the differentiation and re-arranging terms we get

$$
\begin{aligned}
\frac{\partial v}{\partial z} & =\frac{g}{f T} \frac{\partial T}{\partial x}+\frac{v}{T} \frac{\partial T}{\partial z} \\
\frac{\partial u}{\partial z} & =-\frac{g}{f T} \frac{\partial T}{\partial y}+\frac{u}{T} \frac{\partial T}{\partial z}
\end{aligned}
$$

Note: the correction terms are usually neglected.

### 8.12 HW8: : - :, 40 min

### 8.13 Gradient-Wind Balance: : - :, $5 \mathbf{m i n}$

- If the isobars are circular and concentric (Fig. 4.16),

$$
\begin{align*}
\mathbf{u} & =V(r) \mathbf{i}_{\phi}  \tag{8.1}\\
\partial p / \partial \theta & =0 \tag{8.2}
\end{align*}
$$

using $V$ because it's just a speed, not a velocity, and it applies all around each circle.

- The corresponding Coriolis force is

$$
\begin{equation*}
-\rho f \mathbf{k} \times \mathbf{u}=\rho f V \mathbf{i}_{r} \tag{8.3}
\end{equation*}
$$

- The centrifugal term is

$$
\begin{equation*}
\left(\rho V^{2} / r\right) \mathbf{i}_{r} \tag{8.4}
\end{equation*}
$$

- The sum of these forces is in balance with the radial pressure gradient

$$
\begin{equation*}
\frac{V^{2}}{r}+f V=\frac{1}{\rho} \frac{\partial p}{\partial r} \tag{8.5}
\end{equation*}
$$

- Draw circular systems with force term vectors for both rotation directions.
- Low pressure is on the left side of the wind (in the NH), so a low pressure system has counterclockwise (cyclonic) motion.
- A high pressure system has clockwise (anticyclonic) motion.
- If $r$ is large, this reduces to geostrophic balance (weather fronts, hurricanes)
- If $r$ is small, it reduces to cyclostrophic balance (tornadoes, thunderstorms)


### 8.14 Vorticity: : — :, 25 min

- Vorticity is the fluid version of angular velocity
- It refers to the local rotation in the fluid
- Vorticity is the curl of velocity:

$$
\begin{equation*}
\omega=\nabla \times \mathbf{u}=\left(\frac{\partial w}{\partial y}-\frac{\partial v}{\partial z}, \frac{\partial u}{\partial z}-\frac{\partial w}{\partial x}, \frac{\partial v}{\partial x}-\frac{\partial u}{\partial y}\right) \tag{8.6}
\end{equation*}
$$

- For simple, shearless rotation, it is twice the angular velocity
- Think of it like this:
- Look at the last term above, and consider a rotating disk with $v=\omega r$.
- Going horizontally out from the disk center, $\frac{\partial v}{\partial x}$ gives $\omega$
- Going vertically, $\frac{\partial u}{\partial y}$ gives $-\omega$ (right-hand rotation has a negative horizontal velocity for positive $y$ )
- Subtraction makes the $z$ component of curl $\xi=2 \omega$
- There is a curl vector identity in the book that does this in the general sense (i.e., not just for the $z$ component of a disk)
- For large-scale weather systems, it's $\xi$ that matters
- Imagine putting a paddle wheel in the flow. Its turning indicates the amount of vorticity. Note that it's a paddle wheel, not a pinwheel...or anemometer! It's the difference in the strength of flow between the paddles that makes it turn.
- In the diagram below, where is the vorticity positive, negative, or zero?

- There is a special flow, called a point vortex, where $v(r) \propto 1 / r$, that rotates without vorticity.
- In a rotating reference frame, such as the Earth's surface,

$$
\begin{align*}
\mathbf{u}_{a} & =\mathbf{u}_{r}+\boldsymbol{\Omega} \times \mathbf{r}  \tag{8.7}\\
\nabla \times \mathbf{u}_{a} & =\nabla \times \mathbf{u}_{r}+\nabla \times(\boldsymbol{\Omega} \times \mathbf{r})  \tag{8.8}\\
\omega_{a} & =\omega_{r}+2 \boldsymbol{\Omega} \tag{8.9}
\end{align*}
$$

- The vertical component $\xi$ is then:

$$
\begin{align*}
\xi_{a} & =\omega_{a} \cdot \hat{\mathbf{k}}  \tag{8.10}\\
& =\xi_{r}+2 \boldsymbol{\Omega} \cdot \hat{\mathbf{k}}  \tag{8.11}\\
& =\xi_{r}+f  \tag{8.12}\\
f & =2 \Omega \sin \lambda \tag{8.13}
\end{align*}
$$

- $\xi_{a}$ is absolute vorticity
- $\xi_{r}$ is relative vorticity
- $f$ is planetary vorticity, positive in northern hemishphere (NH), negative in southern hemisphere (SH)
- Typically, for large weather systems (away from the equator) $f>\xi_{r}$
- Relative vorticity is positive for counterclockwise rotation everywere
- In NH, positive $\xi_{r}$ is low pressure: hurricanes, etc.
- In SH , hurricanes have negative $\xi_{r} \ldots$ but $f$ is negative there, too, so they act the same


### 8.15 Pressure Coordinates and Geopotential: : - :, 20 min

From the hydrostatic balance we can get

$$
g\left(\frac{\partial z}{\partial p}\right)_{x, y, t}=-\frac{1}{\rho}=-\frac{R T}{p}
$$

and introducing $\Phi=g z$ the geopotential

$$
\frac{\partial \Phi}{\partial p}=-\frac{R T}{p}
$$

is the hydrostatic equation in pressure coordinates. All our governing equations can be translated into the pressure coordinate system using

$$
\frac{\partial}{\partial z}=\frac{\partial p}{\partial z} \frac{\partial}{\partial p} .
$$

In a similar fashion, the equations can be written for different kinds of vertical coordinates.

## Chapter 9

## Chemical Reaction Rates

### 9.1 Check in: : — :, 5 min

- Talk schedule


### 9.2 Chemistry and Physics: : - :, 5 min

- So far, we have treated gases physically
- Chemistry and chemical changes can impact physics in three ways:
- Spectrum's effect on radiative transfer (where light gets absorbed and emitted, causing heating or cooling)
- Reaction heat (like latent heat)
- Changes in molecular weight
- On Earth and all solar-system planets, chemical changes are small
- On hotter worlds, like close-in exoplanets, composition can change from terminator to limb
- This is a developing area!


### 9.3 Questions: : - :, 5 min

- How do we get the gases we get?
- What can we tell about sources and sinks from gases present?
- If you see $\mathrm{O}_{2}$, does that mean life is present?
- How long will it take to fill the $\mathrm{O}_{3}$ hole?
- How does $\mathrm{O}_{3}$ protect us from UV?
- How does $\mathrm{O}_{3}$ photochemistry work to heat the stratosphere?
- Why are other atmospheres' compositions different from ours?
- Given the conditions on (Titan, Venus, Jupiter, Earth, HD 149026b), what would you expect to happen compositionally, and how does that affect the physics?
- What happens after a volcanic eruption or big impact?


### 9.4 What's Easy?: : - :, 5 min

- Principles surprisingly easy
- Reaction rate theory
- Quantum rapidly gives way to classics and stats
- Cross-sections, etc. computed by specialists
- Solid-sphere approximations mostly work fine
- Generally "linear" (superposable) rules
- Interactions clear
- Rate-limiting steps in reaction sequences simplify things


### 9.5 What's Hard?: : — :, 5 min

- Number of possible reactions is insane
- Reaction rates depend on atomic configurations of molecules, including intermediate states
- Reaction rates depend on $T$
- Often hundreds of reactions in a system
- Chances good some reactions in system not measured at your $T$
- $T$ varies, often dramatically, in all real systems
- Steady-state modeling of simple flames difficult
- Real stuff is almost impossible
- Computer time required is high
- Rates vary by many orders of magnitude, require different $\mathrm{d} t$ in computer code
- Small errors can have big effects


### 9.6 Our Approach: : - :, 5 min

- Cover basics
- Discuss simple cases
- Questions?


### 9.7 Thermodynamics: : - :, 10 min

- Consider reaction: $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}+\mathrm{D}$
- In lab: fixed lab vessel, constant $V$, variable $P$
- In atmosphere: "blob", constant $P$, variable $V$
- $V \mathrm{~d} p=0$
- Assuming reversible, $\Delta Q=\Delta H$ is heat into reaction
- $\Delta Q$ is heat, $\Delta H$ is enthalpy of reaction
- $\Delta H<0$ exothermic
- Only $\Delta H$ is measurable, not $H$
- Standard molar enthalpy of formation: enthalpy to form one mole of substance from elements at STP, $\Delta H_{f}^{\theta}$
- Found in tables, small corrections for $P, T$ changes
- So, $\Delta H^{\theta}=\Delta H_{f}^{\theta}(\mathrm{C})+\Delta H_{f}^{\theta}(\mathrm{D})-\Delta H_{f}^{\theta}(\mathrm{A})-\Delta H_{f}^{\theta}(\mathrm{B})$
- Similar formula for $\Delta G=\Delta H-T_{0} \Delta S \leq 0$ (2nd law)
- By minimizing $\Delta G$, can compute ultimate outcome of a reacting system (thermochemical equilibrium or equilibrium chemistry)
- CEA is a public-domain FORTRAN code written at NASA that calculates this
- TEA is an open-source Python code witten at UCF that calculates this


### 9.8 Ozone Example: : - :, 5 min

- Consider $\mathrm{O}+\mathrm{O}+\mathrm{M} \rightarrow \mathrm{O}_{2}+\mathrm{M}$
- M is any air molecule, used for reaction site, can be another $\mathrm{O}_{2}$
- $\Delta H \approx-500 \mathrm{~kJ} / \mathrm{mol}$
- Exothermic, O recombination heats atmosphere
- Reverse reaction requires energy (see HW)
- Notation: $\mathrm{O}_{2}+h \nu \rightarrow 2 \mathrm{O}$


### 9.9 Unimolecular Rate Constant: : - :, 15 min

- How fast are reactions?
- $n_{\mathrm{A}}=[\mathrm{A}]$ number density or concentration
- Consider $\mathrm{A} \rightarrow \mathrm{B}+\mathrm{C}$
- $R_{\mathrm{A}}$ is reaction rate
- Rate of decrease of [A], rate of increase of [B] or [C]
- $R_{\mathrm{A}}=-\frac{\partial[\mathrm{A}]}{\partial t}=\frac{\partial[\mathrm{B}]}{\partial t}=\frac{\partial[\mathrm{C}]}{\partial t}=[\mathrm{A}] k_{\mathrm{A}}$
- $k_{\mathrm{A}}$ is rate coefficient
- Units s ${ }^{-1}$
- Chemical lifetime

$$
\begin{equation*}
\tau_{\mathrm{A}}=\frac{1}{k_{\mathrm{A}}}=\frac{[\mathrm{A}]}{\left|\frac{\partial[\mathrm{A}]}{\partial t}\right|} \tag{9.1}
\end{equation*}
$$

- $k_{\mathrm{A}}$ independent of [A], $t$
- Integrate:

$$
\begin{align*}
\frac{\mathrm{d}[\mathrm{~A}]^{\prime}}{\mathrm{d} t} & =-[\mathrm{A}]^{\prime} k_{\mathrm{A}}  \tag{9.2}\\
\int_{[\mathrm{A}]_{0}}^{[\mathrm{A}]} \frac{\mathrm{d}[\mathrm{~A}]^{\prime}}{[\mathrm{A}]^{\prime}} & =-\int_{0}^{t} k_{\mathrm{A}} \mathrm{~d} t^{\prime}  \tag{9.3}\\
{[\mathrm{A}]=[\mathrm{A}]_{0} e^{-k_{\mathrm{A}} t} } & =[\mathrm{A}]_{0} e^{-t / \tau_{\mathrm{A}}} \tag{9.4}
\end{align*}
$$

- Without resupply, reaction decays exponentially
- $e$-folding time is $\tau_{\mathrm{A}}$


### 9.10 Bimolecular Rate Constant: : - :, 5 min

- $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}+\mathrm{D}$
- $R_{\mathrm{A}}=-\frac{\partial[\mathrm{A}]}{\partial t}=-\frac{\partial[\mathrm{B}]}{\partial t}=\frac{\partial[\mathrm{C}]}{\partial t}=\frac{\partial[\mathrm{D}]}{\partial t}=[\mathrm{A}][\mathrm{B}] k_{\mathrm{AB}}$
$\bullet$

$$
\begin{equation*}
\tau_{\mathrm{A}}=\frac{1}{[\mathrm{~B}] k_{\mathrm{AB}}}=\frac{[\mathrm{A}]}{\left|\frac{\partial[\mathrm{A}]}{\partial t}\right|} \tag{9.5}
\end{equation*}
$$

- BUT, only get exponential solution above if $[\mathrm{B}] \gg[\mathrm{A}]$


### 9.11 Simultaneous Loss Reactions: : — :, $5 \mathbf{m i n}$

- $\mathrm{A} \rightarrow$ products $\left(k_{1}\right)$
- $\mathrm{A}+\mathrm{B} \rightarrow$ products $\left(k_{2}\right)$
- $\mathrm{A}+\mathrm{C}+\mathrm{D} \rightarrow$ products $\left(k_{3}\right)$
- $R_{\mathrm{A}}=-\frac{\partial[\mathrm{A}]}{\partial t}=[\mathrm{A}] k_{1}+[\mathrm{A}][\mathrm{B}] k_{2}+[\mathrm{A}][\mathrm{C}][\mathrm{D}] k_{3}$
- 

$$
\begin{equation*}
\tau_{\mathrm{A}}=\frac{[\mathrm{A}]}{\left|\frac{\partial[\mathrm{A}]}{\partial t}\right|}=\frac{1}{k_{1}+[\mathrm{B}] k_{2}+[\mathrm{C}][\mathrm{D}] k_{3}} \tag{9.6}
\end{equation*}
$$

A decays if [B], [C], [D] ~constant

- $\tau_{\mathrm{A}}$ still good for instantaneous rate if not


### 9.12 Simultaneous Loss and Gain Reactions: : - :, 5 min

- $\mathrm{E}+\mathrm{F} \rightarrow \mathrm{A}+\mathrm{G}\left(k_{4}\right)$
- $R_{\mathrm{A}}=-\frac{\partial[A]}{\partial t}=[\mathrm{A}] k_{1}+[\mathrm{A}][\mathrm{B}] k_{2}+[\mathrm{A}][\mathrm{C}][\mathrm{D}] k_{3}-[\mathrm{E}][\mathrm{F}] k_{4}$
- Equillibrium now possible! Set $\frac{\partial[A]}{\partial t}=0$

$$
\begin{equation*}
[\mathrm{A}]=\frac{[\mathrm{E}][\mathrm{F}] k_{4}}{k_{1}+[\mathrm{B}] k_{2}+[\mathrm{C}][\mathrm{D}] k_{3}} \tag{9.7}
\end{equation*}
$$

- All this assumes constant volume, else modify for motion.


## Chapter 10

## Chemical Reactions

### 10.1 Check in: : - :, 5 min

### 10.2 Physics of Reactions: : - :, $15 \mathbf{m i n}$

- Consider $\mathrm{A}+\mathrm{BC} \rightarrow(\mathrm{ABC}) \rightarrow \mathrm{AB}+\mathrm{C} r_{\mathrm{AB}} r_{\mathrm{bc}}$
- 3 particles in mutual potential wells (Andrews Fig. 6.2)
- B moves from C to A
- Must climb out of potential well of C
- Then falls into well of A
- Initially wavefunction confined to C's area
- Receives energy (photon or collision)
- If enough to get out of well, wavefunction spans both wells
- Prob of being in deeper well much greater
- Next collapse of states (photon or collision), localizes
- Usually localizes to A’s deeper well
- Taken as population, draw as activation energy (Andrews Fig. 6.3)
- Activation energy $E_{1}=H_{\mathrm{ABC}}-H_{\mathrm{A}+\mathrm{BC}}$
- Regained energy $E_{2}=H_{\mathrm{ABC}}-H_{\mathrm{AB}+\mathrm{C}}$
- Enthalpy of reaction $\Delta H=E_{1}-E_{2}=H_{\mathrm{AB}+\mathrm{C}}-H_{\mathrm{A}+\mathrm{BC}}<0$ is exothermic
- Reverse reaction is endothermic, takes energy


### 10.3 Collision Theory: : - :, 20 min

- What does reaction rate depend on?
- Geometric theory is good at most temps in atmospheres
- Collisions/volume/time $=[\mathrm{A}][\mathrm{BC}] \sigma \bar{c}$
- Collision cross-section $\sigma=\pi\left(r_{\mathrm{A}}+r_{\mathrm{bc}}\right)^{2}$
- $r_{\mathrm{A}}$ and $r_{\mathrm{BC}}$ are radii of "notional" hard spheres
- Chosen to make this model work for all reactions involving them
- Not bad approximations for sizes of their wavefunctions' high-probability regions
- Mean relative speed of molecules is at temperature $T$ :
$\bar{c}=\left(\frac{8 k T}{\pi m_{\mathrm{r}}}\right)^{1 / 2}$
- Particle masses are $m_{\mathrm{A}}$ and $m_{\mathrm{BC}}$
- System reduced mass is $m_{\mathrm{r}}=\frac{m_{\mathrm{A}} m_{\mathrm{BC}}}{m_{\mathrm{A}}+m_{\mathrm{BC}}}$
- Which collisions produce reaction?
- Statmech says probability of reaction $=e^{-E_{1} /(k t)}$
- Loss rate of A is thus $-\frac{\partial[\mathrm{A}]}{\partial t}=[\mathrm{A}][\mathrm{BC}] \pi\left(r_{\mathrm{A}}+r_{\mathrm{bc}}\right)^{2}\left(\frac{8 k T}{\pi m_{\mathrm{r}}}\right)^{1 / 2} e^{-E_{1} /(k t)}=k_{2}[\mathrm{~A}][\mathrm{BC}]$
- Similar to empirical Arrhénius expression $k_{2}=\alpha e^{-E_{a} /(k t)}$
- (except weak $T^{1 / 2}$ dependence)


### 10.4 Photodissociation: : - :, 20 min

- In photodissociation, we have $\mathrm{A}+h \nu \rightarrow$ products
- $\frac{\partial[A]}{\partial t}=-j_{\mathrm{A}}[A]$
- If no other processes, implies [A] decrease as $e^{-j_{\mathrm{A}} t}$
- $j_{\mathrm{A}}$ depends on spectrum and intensity of sunlight and properties of [A]
- Between $\nu$ and $\nu+\mathrm{d} \nu$ the probability density is $\mathrm{d} j_{\mathrm{A} \nu}=\Phi_{\mathrm{A} \nu} \sigma_{\mathrm{A} \nu}\left(\frac{F_{\nu}^{\downarrow}}{h \nu}\right) d \nu$
- Start with reaction outcome vs. $\nu$
- $\Phi_{\mathrm{A} \nu}=$ Expected number of A gotten per photon at frequency $\nu$
- $\Phi_{\mathrm{A} \nu} \approx 0$ at low $\nu$
- At $h \nu>E_{1}, \Phi_{\mathrm{A} \nu} \approx 1$
- $\sigma_{\mathrm{A} \nu}$ is absorption cross-section per molecule
- Related to absorption coefficient $k$, varies strongly with $\nu$
- $\frac{F_{\nu}^{\downarrow}}{h \nu}$ is the flux in number of photons at a given energy
- Depends on absorbing gases in solar beam
- Total photodissociation rate is integral over $\nu$
- $j_{\mathrm{A}}=\int_{\nu_{0}}^{\infty} \Phi_{\mathrm{A} \nu} \sigma_{\mathrm{A} \nu} \frac{F_{\nu}^{\downarrow}}{h \nu} \mathrm{~d} \nu$
- Heating rate enters through quantum yield $\Phi_{\mathrm{A} \nu}=\frac{\text { consumption of dissociation energy }}{\text { heating rate }}$
- Dissociation energy used $=\mathrm{d} j_{\mathrm{A} \nu}[\mathrm{A}] h \nu$
- Heating rate per unit volume $=\rho Q_{\mathrm{A} \nu} \mathrm{d} \nu$
- So, first layer to have sufficient density of absorber may get all the flux at its frequencies
- Leaves no flux for deeper absorbers to see
- Forms heating layers like ozone layer


### 10.5 Equilibrium Chemistry on Giant Planets: : - :, 25 min

- Consider an atomic composition, such as solar composition
- At a given $P, T$, equilibrium chemistry gives a molecular composition
- This leads to abundance diagrams, colloquially known as "spaghetti plots"
- Note how certain chemicals pick up as others drop
- This is due to competition for a key atom, like carbon
- For solar abundance, there is enough hydrogen to fill all demand
- He does nothing but decrease the partial pressures of everything else at a given pressure
- At high enrichment (increase everything except H and He ), there is competition for H
- The sun has $[\mathrm{C}] /[\mathrm{O}]=0.55$, so it is O-rich, and C is the key atom
- If the air is C-rich, O becomes the key atom, and the chemistry changes a lot!
- Now, consider a hot planet that is cooler at the limb.
- Calculate temperatures with rule like instantaneous reradiation
- Or, use a GCM's output
- Pick the abundances from the spaghetti plots
- Color-code a diagram of the planet, with red $=[\mathrm{CO}]$, green $=\left[\mathrm{CH}_{4}\right.$, blue $=\left[\mathrm{H}_{2} \mathrm{O}\right]$
- Log-scale the abundances to range 0-255
- Can see how much chemistry (and therefore spectrum) changes on planet
- This affects observable/retrievable spectrum
- Can a disk-integrated spectrum stand in for the whole planet?
- Can anything representative be recovered from one?
- Does spatially differential atmospheric heating change the dynamics?

