Final Review

AOSC / CHEM 433 & AOSC 633

Ross Salawitch & Walt Tribett

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2019

Lecture 24 14 May 2019

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Course Logistics



Chemistry in Context : Applying Chemistry to Society, 7/e

American Chemical Society (ACS) Catherine H. Middlecamp, University of Wisconsin--Madison Steven W. Keller, University of Missouri--Columbia Karen L. Anderson, Madison Area Technical College Anne K. Bentley, Lewis & Clark College Michael C. Cann, University of Scranton Jamie P. Ellis, The Scripps Research Institute

The author team truly benefitted from the expertise of a wider community. We extend our thanks to the following individuals for the technical expertise they provided to us in preparing the manuscript:

Mark E. Anderson, University of Wisconsin–Madison David Argentar, Sun Edge, LLC Marion O'Leary, Carnegie Institution for Science Ross Salawitch, University of Maryland Kenneth A. Walz, Madison Area Technical College

If you've rented, *please bring with you to final exam, on Mon 20 May, 10:30 am* (this room)

Of the "nine ways to cool the planet" discussed in the IEEE article, which of these seems most appealing to you? Briefly state why.



9 ideas:

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Pacala and Socolow: CO₂ Stabilization Wedges

Humanity already possesses the fundamental scientific, technical, and industrial know-how to solve the carbon and climate problem for the next half-century. A portfolio of technologies now exists to meet the world's energy needs over the next 50 years and limit atmospheric CO_2 to a trajectory that avoids a doubling of the preindustrial concentration. Every element in this portfolio has passed beyond the laboratory bench and demonstration project; many are already implemented somewhere at full industrial scale. Although no element is a credible candidate for doing the entire job (or even half the job) by itself, the portfolio as a whole is large enough that not every element has to be used.



Pacala and Socolow, Science, 2004 (Aux reading, Lecture 18)

Pacala and Socolow: CO₂ Stabilization Wedges

| Action | Details |
|---|--|
| Economy-wide carbon-intensity Increase reduction (emissions/\$GDP) (e.g., ir vear to | Energy efficiency and conservation reduction by additional 0.15% per year crease U.S. goal of 1.96% reduction per 2.11% per year) |
| 1. Efficient vehicles Increase 60 mp | uel economy for 2 billion cars from 30 to |
| 2. Reduced use of vehicles Decrease 10,000 | car travel for 2 billion 30-mpg cars from to 5000 miles per year |
| 3. Efficient buildings Cut carbo and ap | n emissions by one-fourth in buildings pliances projected for 2054 |
| 4. Efficient baseload coal plants Produce 1 insteac today) | wice today's coal power output at 60% of 40% efficiency (compared with 32% |
| 5. Gas baseload power for coal Replace 1 baseload power gas pla gas-baseload | 400 GW 50%-efficient coal plants with nts (four times the current production of sed power) |
| C. Continue CO. at baseland names | CO ₂ Capture and Storage (CCS) |
| plant gas (cc | mpared with 1060 GW coal in 1999) |
| 7. Capture CO ₂ at H ₂ plant Introduce from c (compa sources | CCS at plants producing 250 MtH ₂ /year oal or 500 MtH ₂ /year from natural gas ared with 40 MtH ₂ /year today from all ;) |
| 8. Capture CO ₂ at coal-to-synfuels Introduce plant million if half capture | CCS at synfuels plants producing 30 barrels a day from coal (200 times Sasol), of feedstock carbon is available for |
| Geological storage Create 3 | 500 Sleipners |

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Pacala and Socolow: CO₂ Stabilization Wedges

| Action | Details |
|--|---|
| | Nuclear fission |
| 9. Nuclear power for coal power | Add 700 GW (twice the current capacity) |
| 10. Wind power for coal power | <i>Renewable electricity and fuels</i> Add 2 million 1-MW-peak windmills (50 times the current capacity) "occupying" 30 × 10 ⁶ ha, on land or offshore |
| 11. PV power for coal power | Add 2000 GW-peak PV (700 times the current capacity) on 2 $	imes$ 10 6 ha |
| Wind H₂ in fuel-cell car for gasoline in hybrid car | Add 4 million 1-MW-peak windmills (100 times the current capacity) |
| 13. Biomass fuel for fossil fuel | Add 100 times the current Brazil or U.S. ethanol production, with the use of 250 $	imes$ 10 ⁶ ha (one-sixth of world cropland) |
| Reduced deforestation, plus reforestation, afforestation, and new plantations. Conservation tillage | Forests and agricultural soils Decrease tropical deforestation to zero instead of 0.5 GtC/year, and establish 300 Mha of new tree plantations (twice the current rate) Apply to all cropland (10 times the current usage) |

Final Exam

- Monday, 20 May, 10:30 am to 12:30 pm
- This room
- Format similar to prior exams
- "Virtual conversation"
- Closed book, no notes, no calculator
- Backbone of course remains the lectures
- Entire course will be covered on the final exam
- Please ask if you think a question requires clarification
- If you have an exam either right before or right after this exam, please let me and Walt know ASAP

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Greenhouse Effect



What is the most important greenhouse gas (GHG) ?

FAQ 1.3, Figure 1. An idealised model of the natural greenhouse effect. See text for explanation.

Question 1.3, IPCC, 2007

Radiative Forcing of Climate, 1750 to 2011



Figure 1.4, Paris Beacon of Hope

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FAQ 1.1, Figure 1. Estimate of the Earth's annual and global mean energy balance. Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere is balanced by the Earth and atmosphere releasing the same amount of outpoing longwave radiation. About half of the incoming solar radiation is absorbed by the Earth's surface. This energy is transferred to the atmosphere by warming the air in contact with the surface (thermals), by evapotranspiration and by longwave radiation that sobscrede by clouds and greenhouse gases. The atmosphere in turn radiates longwave energy back to Earth as well as out to space. Source: Kiehl and Tenberth (1997).

Question 1.1, IPCC, 2007

Radiative Forcing of Climate is Change in Energy reaching the lower atmosphere (surface to tropopause) as GHGs rise. "Back Radiation" is most important term.

GWP – Global Warming Potential

$$\text{GWP}(\text{CH}_4) = \frac{\int_{\text{time initial}}^{\text{time final}} a_{\text{CH4}} \times [\text{CH}_4(t)] \text{ dt}}{\int_{\text{time final}}^{\text{time final}} a_{\text{CO2}} \times [\text{CO}_2(t) \text{ dt}]}$$

where:

 a_{CH4} = Radiative Efficiency (W m⁻² ppb⁻¹) due to an increase in CH₄

 $a_{\rm CO2}$ = Radiative Efficiency (W m⁻² ppb⁻¹) due to an increase in CO₂

 $CH_4(t)$ = time-dependent response to an instantaneous release of a pulse of CH_4

 $CO_2(t)$ = time-dependent response to an instantaneous release of a pulse of CO_2

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GWP – Global Warming Potential

SAR: Second Assessment Report (issued in 1995)

Table TS.2. Lifetimes, radiative efficiencies and direct (except for CH₂) global warming potentials (GWP) relative to CO₂. {Table 2.14}

| Industrial Designation | Badiative | | | Global Warming Potential for Given Time Horizon | | | |
|---------------------------|------------------|------------------------|---|--|-------|--------|--------|
| or Common Name (years) | Chemical Formula | Lifetime (years) | Efficiency (W m ⁻² ppb ⁻¹⁾ | SAR‡ (100-yr) | 20-yr | 100-yr | 500-yr |
| Carbon dioxide | CO ₂ | See below ^a | ^b 1.4x10 ^{−5} | 1 | 1 | 1 | 1 |
| Methanec | CH ₄ | 12° | 3.7x10−4 | 21 | 72 | 25 | 7.6 |
| Nitrous oxide | N ₂ O | 114 | 3.03x10 ⁻³ | 310 | 289 | 298 | 153 |

Notes:

[‡] SAR refers to the IPCC Second Assessment Report (1995) used for reporting under the UNFCCC.

^a The CO₂ response function used in this report is based on the revised version of the Bern Carbon cycle model used in Chapter 10 of this report (Bern2.5CC; Joos et al. 2001) using a background CO₂ concentration value of 378 ppm. The decay of a pulse of CO₂ with time t is given by

 $a_0 + \sum_{i=1}^{3} a_i \cdot e^{-t/\tau_i}$ where $a_0 = 0.217$, $a_1 = 0.259$, $a_2 = 0.338$, $a_3 = 0.186$, $\tau_1 = 172.9$ years, $\tau_2 = 18.51$ years, and $\tau_3 = 1.186$ years, for t < 1,000 years.

^b The radiative efficiency of CO₂ is calculated using the IPCC (1990) simplified expression as revised in the TAR, with an updated background concentration value of 378 ppm and a perturbation of +1 ppm (see Section 2.10.2).

^c The perturbation lifetime for CH₄ is 12 years as in the TAR (see also Section 7.4). The GWP for CH₄ includes indirect effects from enhancements of ozone and stratospheric water vapour (see Section 2.10).

from IPCC 2007 "Physical Science Basis"

Time constant of 172.9 years dominates

GWP - Global Warming Potential



 $\begin{array}{l} \text{CO}_2 - \text{equivalent emissions} = \text{ Emissions of CO}_2 + \\ & \text{Emissions of CH}_4 \times \text{GWP of CH}_4 + \\ & \text{Emissions of N}_2\text{O} \times \text{GWP of N}_2\text{O} + \\ & \text{etc.} \end{array}$

Commonly, GWPs on 100 year time horizon are used although entities such as the Sierra Club prefer the 20 year time horizon

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Connection Between GHG Abundance and Surface T

How much does ΔF change when CO₂ changes?

$$\Delta F \approx 5.35 \text{ W/m}^2 \ln \left(\frac{\text{CO}_2^{\text{Final}}}{\text{CO}_2^{\text{Initial}}} \right)$$

Changes in ΔF can be caused by changes in chemical composition (GHGs), aerosol loading, as well as surface albedo, H₂O, & cloud feedback

$$\Delta T = \lambda_{BB} (1 + f) (\Delta F_{CO2} + \Delta F_{CH4+N2O} + \Delta F_{ALBEDO} + \Delta F_{AEROSOLS})$$

where $\lambda_{BB} = 0.3 \text{ K} / \text{W m}^{-2}$,

and f = represents total feedbacks due to surface albedo, H₂O, & clouds

Connection Between GHG Abundance and Surface T

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 $\Delta T = \lambda_{BB} (1 + f) (\Delta F_{CO2} + \Delta F_{CH4+N2O} + \Delta F_{ALBEDO} + \Delta F_{AEROSOLS})$ where $\lambda_{BB} = 0.3 \text{ K} / \text{W m}^{-2}$, and f = represents total feedbacks due to surface albedo, H₂O, & clouds

Climate models that consider water vapor & lapse rate (LR) feedback find:

 $feedback_{H2O\&LR} = 0.45$

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https://www.atmos-chem-phys.net/13/3997/2013/acp-13-3997-2013.html updated by Austin Hope & Laura McBride



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Arctic Sea Ice: Canary of Climate Chnage





https://nsidc.org/arcticseaicenews/2018/10/september-extent-ties-for-sixth-lowest/

Arctic Sea Ice: Canary of Climate Chnage



- In 2004, 25% of monitored polar bears made a long-distance swim
- In 2012, 69% of monitored polar bears made a long-distance swim
- During long swims, adult bears will lose significant body weight and cubs will die

Source: https://www.washingtonpost.com/news/speaking-of-science/wp/2016/04/21/melting-arctic-ice-is-forcing-polar-bears-to-swim-for-more-than-a-week-without-rest

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The Ozone Hole may have shielded the Antarctic from warming



Simulated and observed changes in surface temperature (K) and winds from 1969 to 2000, averaged over December to May.

Gillett and Thompson, Science, 2003

Ozone Depletion Potential and Halocarbons

ODP (species "i") =

continuous

Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

| halogen source & HFC substitute gases. | | | global loss of O_{2} due to unit mass emission of " <i>i</i> " | | | | | |
|---|---------------------------------|--------------------------------------|--|--|--|--|--|--|
| Gas | Atmospheric Lifetime (years) | Ozone Depletion Potential (ODP) ° | $\frac{1}{g}$ global loss of O_2 due to unit mass emission of CFC-11 | | | | | |
| Halogen source gases | | | | | | | | |
| Chlorine gases ^e | | | $(\alpha n_{\rm Br} + n_{\rm Cl}) = \tau_i = MW_{\rm CFC-11}$ continuous | | | | | |
| CFC-11 | 52 | 1 | $\approx \frac{1}{2} \frac{1}{\tau} \frac{1}{\tau} \frac{1}{MW}$ | | | | | |
| CFC-12 | 102 | 0.73 | $J \qquad l_{CFC-11} \qquad NI W_i$ | | | | | |
| CFC-113 | 93 | 0.81 | where . | | | | | |
| Carbon tetrachloride (CCl ₄) | 26 | 0.72 | τ is the global atmospheric lifetime | | | | | |
| HCFCs | 1-18 | 0.01-0.10 | | | | | | |
| Methyl chloroform (CH ₃ CCl ₃) | 5 | 0.14 | MW is the molecular weight | | | | | |
| Methyl chloride (CH ₃ Cl) | 0.9 | 0.015 | WW is the molecular weight | | | | | |
| Very short-lived Cl-containing gases | less than 0.5 | b.d very low | <i>n</i> is the number of chlorine or bromine atoms | | | | | |
| Bromine gases | | | | | | | | |
| Halon-1301 | 72 | 15.2 | α is the effectiveness of ozone loss by bromin | | | | | |
| Halon-1211 | 16 | 6.9 | relative to ozone loss by chlorine | | | | | |
| Methyl bromide (CH ₃ Br) | 0.8 | 0.57 | | | | | | |
| Hydrofluorocarbons (HFCs) | | | $\alpha = 60$ | | | | | |
| HFC-134a | 14 | 0 🔨 | Bromine molecules are about 60 times more damaging | | | | | |
| HFC-23 | 228 | 0 | to the ozone layer than chloring molecules | | | | | |
| HFC-143a | 51 | 0 | to the ozone layer than chiorne molecules | | | | | |
| HFC-125 | 31 | 0 | HFCs (anthropogenic halocarbons | | | | | |
| HFC-152a | 1.6 | 0 | containing only <u>fluorine</u> , carbon, and | | | | | |
| HFC-32 | 5.4 | 0 | hydrogen) and thus pose no threat | | | | | |
| | | | to the ozone layer | | | | | |

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Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

- a) What type of aerosol particles are present in the mid-latitude stratosphere (i.e., what is the chemical composition of these aerosols?)
- b) What heterogeneous chemical reaction occurs on the aerosol particles present in the mid-latitude stratosphere and how is the abundance of CIO affected by this reaction?
- c) What type of particles are present in the polar stratosphere during winter (i.e., what are these particles called and what is the chemical composition of a "common type" of these particles?)
- d) What is the effect of these particles on the chemical composition of the polar stratosphere? Scientists have shown that chemical reactions occurring on the surface of these particles convert species such as (that do not deplete ozone) that, while reactive, and and do not not cause harm to the ozone layer during the darkness of winter.
- e) Following the return of sunlight, significant levels of what radical compound builds up inside the Antarctic stratosphere, leading to rapid loss of ozone? Hint: we're looking for a monoxide
- f) Why does the ozone hole occur only over Antarctica?

Earth's Atmosphere – Effect of Humans

Stratospheric Ozone – shields surface from solar UV radiation



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Climate and Chemistry Coupling

Scientists have long known that rising GHGs leads to cooling of the stratosphere, due to direct radiative effects

The stratosphere has been cooling past several decades in a manner broadly consistent with theory:



Figure 4–11, WMO/UNEP (2011)

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Future Trends, Upper Stratospheric Ozone



Oman et al., JGR, 2010

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Future Trends, Upper Stratospheric Ozone



Rosenfield et al., JGR, 2002



One Atmosphere – One Photochemistry



Troposphere



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Tropospheric Ozone Production

 $CO + OH \rightarrow CO_2 + H$ $H + O_2 + M \rightarrow HO_2 + M$ $HO_2 + NO \rightarrow OH + NO_2$ $NO_2 + h\nu \rightarrow NO + O$ $O + O_2 + M \rightarrow O_3 + M$

Net: $CO + 2O_2 \rightarrow CO_2 + O_3$

"Chain Mechanism" for production of ozone

Initiation: O_3 photolysis giving $O({}^1D)$, followed by $H_2O+O({}^1D) \rightarrow 2OH$ as well as emission of CO & NO_x from combustion of fossil fuels Termination: $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ or $OH + NO_2 + M \rightarrow HNO_3 + M$ Propagation: $HO_2 + NO$ Ozone Production "limited" by k[HO₂][NO] (propagation term) High NO_x (NO+NO₂) forces termination via production of HNO_3 . In this case, as NO_x rises, OH and HO_2 (HO_x) fall \Rightarrow what happens to O_3 production ?

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Tropospheric Ozone Production

 $\begin{array}{c} \mathrm{CO} + \mathrm{OH} \ \rightarrow \mathrm{CO}_2 + \mathrm{H} \\ \mathrm{H} + \mathrm{O}_2 + \mathrm{M} \ \rightarrow \mathrm{HO}_2 + \mathrm{M} \\ \mathrm{HO}_2 + \mathrm{NO} \ \rightarrow \mathrm{OH} + \mathrm{NO}_2 \\ \mathrm{NO}_2 + \mathrm{hv} \ \rightarrow \mathrm{OH} + \mathrm{NO}_2 \\ \mathrm{OO}_2 + \mathrm{hv} \ \rightarrow \mathrm{OO}_3 + \mathrm{M} \end{array}$

Net: $CO + 2O_2 \rightarrow CO_2 + O_3$

Ozone Production "limited" by $k[HO_2][NO]$ (propagation term) High NO_x (NO+NO₂) forces termination via production of HNO₃.

In this case, as NO_x rises, OH and HO₂ (HO_x) fall

⇒ what happens to O₃ production ?



Dramatic Improvements Local Air Quality, Past 4 Decades



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Day-to-day meteorology (weather!) affects severity and duration of pollution episodes



http://www.mde.state.md.us/assets/document/BJH%20-%20Basics%20on%20Ozone%20Transport.ppt



http://www.ux1.eiu.edu/~cfjps/1400/FIG07_014A.jpg

http://www.fas.org/irp/imint/docs/rst/Sect14/jet_stream.jpg

Subtropical Jet: where poleward descending branch of the Hadley Circulation meets the equatorward descending of the Ferrel Cell

Area of high pressure, fair weather, low rainfall: conductive to high ozone

Poleward expansion of the sub-tropical jet:

- Number of days Subtropical Jet within 150 miles of Baltimore has increased by ~50% between 1979 and 2003 due to "frontal movement"
- Driving force: weakening of the equator to pole temperature gradient, caused by more rapid warming at high latitudes compared to tropics

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SpeciesSourceConsequenceCO2CH4N2ONOxSO2SotFCSHalonsHFCS

Our Favorite Air Pollutants 😊

Final Statements

We're on the path to more use of renewables:

United States electricity Net generation for all sectors, monthly



but how do we extend the transition away from fossil fuels to more sectors, and move more quickly?

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Final Statements

It is difficult for people living now, who have become accustomed to the steady exponential growth in the consumption of energy from fossil fuels, to realize how transitory the fossil fuel epoch will eventually prove to be when it is viewed over a longer span of human history

> M. King Hubbert, Scientific American, 1971 as quoted in foreword of *When Oil Peaked* by Kenneth S. Deffeyes

In many ways, fossil fuels should be considered as a gift from nature, which have allowed mankind to reach unprecedented levels of development. They served us well, but now – due to their finite nature – must be replaced by more sustainable sources of energy.

Olah et al., Beyond Oil and Gas: The Methanol Economy, 2009.