Radiative Forcing AOSC / CHEM 433 & AOSC 633 Ross Salawitch & Walt Tribett

Goals:

- Understanding interaction between gases and IR radiation
- Radiative forcing of greenhouse gases
- · Radiative forcing of aerosols

Lecture 7 20 February 2019

Copyright © 2019 University of Maryland. This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch.

ΔRF of Climate



1

Announcements

- Will hold problem set reviews during various evenings
 - Problem Set #1: Monday, 25 Feb or Tues 26 Feb
 - 5 pm? 6 pm? 7 pm?
 - We will hand out solutions at the review; no credit for P Set #1 after review
- Problem Set #2 due Thurs, 28 Feb; will be posted this evening
 - Will review on Mon, 4 Mar (day before exam)
 - No late penalty for P Set #2 but must be turned in prior to start of revie to receive credit
 - If turned in by 28 Feb, or soon thereafter, will return graded P Set at review
- First exam is Tues, 5 Mar, in class:
 - Closed book, no calculator or e-device
 - Will focus on concepts rather than calculations
 - New exams every year; will review prior exam in class on 28 Feb to help you prepare

3

CH₄ is lost by reaction with OH

OH is present at the sub parts per trillion (1 part in 10¹²) level and highly reactive: major challenge to measure

We can calculate OH in global models



Lifetime of CH₄ =
$$\frac{1}{k[OH]} = \frac{1}{3.59 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1} \times 1 \times 10^6 \text{ molec cm}^{-3}}$$

= 2.79×10⁸ sec = 8.8 yr

Copyright © 2019 University of Maryland.

This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch.

CH₄ is lost by reaction with OH

CH₄ is present at the parts per million (1 part in 10⁶) level and stable, therefore, much more straight forward to measure



https://www.esrl.noaa.gov/gmd/hats/flask/camp.html

Copyright © 2019 University of Maryland. This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch.

5





Viewed from space and averaged over space and time, Earth emits \sim 238 W/m² of thermal radiation between wavelengths of 5 and 50 μ m.

The terrestrial emission spectrum matches that of a combination of blackbody spectra of temperatures between 220 and 320K.

The four most important gases that absorb terrestrial radiation (H₂O, CO₂, CH₄, O₃) are noted.



Hanel et al., JGR, 1972: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/JC077i015p02629

Copyright © 2019 University of Maryland. This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch.



FIGURE 3.4.5 Overview of the earth's outgoing infrared radiation as a function of wave number (the inverse of wavelength) and latitude.⁴³ Radiances for this figure were calculated using Modtran and a web interface developed by David Archer available here: http://climatemodels.uchicago.edu/modtran/.

Kirk-Davidoff, Chapter 3.4, Green Chemistry: An Inclusive Approach, 2018

- GHGs prevent outgoing energy emitted from the surface from being released back into space, thereby trapping this energy and releasing it in the form of heat.
- Averaged over space and time, the Earth radiates to space an amount of energy consistent with that of a black body at 255 K.
- Some spectral regions are nearly filled (i.e., 667 cm⁻¹) whereas many others exhibit negligible attenuation of outgoing radiation.
- A newly discovered "miracle compound" with a long atmospheric lifetime will be much more damaging to Earth's climate system if it absorbs in a region that is _____, rather than a region that is _____.

7

Global Warming Potential

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

Table 3.2	Examples of Greenhouse Gases						
Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	GI	Global Warming Potential	
carbon dioxide CO ₂	270 ppm	388 ppm	50-200*	Fossil fuel combustion, deforestation, cement production		1	
methane CH ₄	700 ppb	1760 ppb	12	Rice paddies, waste dumps, livestock		21	
nitrous oxide N ₂ O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	_	310	
CFC-12 CCl ₂ F ₂	0	0.56 ppb	102	Liquid coolants, foams		8100	

*A single value for the atmospheric lifetime of CO₂ is not possible. Removal mechanisms take place at different rates. The range given is an estimate based on several removal mechanisms.

Chapter 3, Chemistry in Context

100 year time horizon

Some GHGs are much more effective than others, in terms of GWP (i.e., perturbation of RF per mass)

Copyright © 2019 University of Maryland. This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch.

9

Atmospheric Radiation

- Solar irradiance (downwelling) at top of atmosphere occurs at wavelengths between ~200 and 2000 nm (~5750 K "black body" temperature)
- Thermal irradiance (upwelling) at top of the atmosphere occurs at wavelengths between ~5 and 50 μ m (~245 K "black body" temperature)



- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration of electrons) of molecules
- Absorption and re-emission in the IR occurs due to changes in vibrational and rotational states of molecules with electric dipole moments

Radiation & Molecules

Radiation can induce photo-dissociation (March 12 lecture), vibration, and rotation of molecules.



Fig 3.19, Chemistry in Context

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

11

Radiation & Molecules

Radiation can induce photo-dissociation (March 12 lecture), vibration, and rotation of molecules.

Thermal IR radiation is not energetic enough to break molecular bonds (i.e., photo-dissociate). Upon absorption, thermal IR will increase the vibrational energy of a molecule

 CO_2 (linear molecule) has 4 vibrational modes (see below): for molecules vibrational frequencies are quantized. That is, only certain energies for the system are allowed. Most importantly, only photons with certain wavelengths (energies) will excite molecular vibrations.



Fig 3.16, Chemistry in Context

Radiation & Molecules

Radiation can induce photo-dissociation (March 12 lecture), vibration, and rotation of molecules.

Thermal IR radiation is not energetic enough to break molecular bonds (i.e., photo-dissociate). Upon absorption, thermal IR will increase the vibrational energy of a molecule

CO₂ (linear molecule) has 4 vibrational modes (see below): for molecules vibrational frequencies are quantized. That is, only certain energies for the system are allowed. Most importantly, only photons with certain wavelengths (energies) will excite molecular vibrations.



http://science.widener.edu/svb/ftir/ir co2.html

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

13

Excitation of Molecules

A greenhouse gas must have either

- naturally occurring dipole moment
- exhibit a dipole moment during vibration

Dipole moment ⇒ product of magnitude of charges & distance of separation between charges: i.e., a molecule is said to have a dipole moment if it has a non-zero spatial distribution of charge

No dipole moment, either naturally or during vibration:



:N≡N: ∷́0=0:

A greenhouse gas must have either

- naturally occurring dipole moment
- exhibit a dipole moment during vibration

Dipole moment ⇒ product of magnitude of charges & distance of separation between charges: i.e., a molecule is said to have a dipole moment if it has a non-zero

spatial distribution of charge

CO₂ has ho natural dipole moment



Fig 3.14, Chemistry in Context

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

15

Excitation of Molecules

A greenhouse gas must have either

- · naturally occurring dipole moment
- · exhibit a dipole moment during vibration

Symmetric Stretch: no dipole moment





A greenhouse gas must have either

- naturally occurring dipole moment
- exhibit a dipole moment during vibration

Anti-symmetric stretch

Anti-symmetric Stretch: dipole moment



Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

17

Excitation of Molecules

A greenhouse gas must have either

- naturally occurring dipole moment
- exhibit a dipole moment during vibration

spatial distribution of charge



http://www.vidyarthiplus.in/2013/12/cy6151-engineering-chemistry-1.html#.VOUqai4RXIY

Wavenumber = 1 / Wavelength

1 / 2350 cm⁻¹ = 4.25×10⁻⁴ cm = 4.25×10⁻⁶ m = 4.25 μ m 1 / 666 cm⁻¹ = 1.50×10⁻³ cm = 15.0×10⁻⁶ m = 15.0 μ m



Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

19

Excitation of Molecules

A greenhouse gas must have either

- · naturally occurring dipole moment
- exhibit a dipole moment during vibration

CH₄ also has no natural dipole moment: charge is uniformly distributed



Figs 3.10 & 3.11, Chemistry in Context



This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

A greenhouse gas must have either

- naturally occurring dipole moment
- exhibit a dipole moment during vibration

CH₄ has 4 unique vibrational modes, 2 of which interact with the IR field



http://www2.ess.ucla.edu/~schauble/MoleculeHTML/CH4_html/CH4_page.html

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

21

Excitation of Molecules

A greenhouse gas must have either

- · naturally occurring dipole moment
- · exhibit a dipole moment during vibration

H₂O has a natural dipole moment (bent molecule) and absorbs in three spectral regions:



http://www2.ess.ucla.edu/~schauble/MoleculeHTML/H2O html/H2O page.html

A greenhouse gas must have either

- naturally occurring dipole moment
- exhibit a dipole moment during vibration

N_2O also has a natural dipole moment (since it is an asymmetric molecule) and also absorbs in three spectral regions:



http://www2.ess.ucla.edu/~schauble/MoleculeHTML/N2O html/N2O page.html

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

23



Absorption vs. Wavelength

Fig 2.6, IPCC SROC (Special Report on Ozone layer and Climate), 2005 https://www.ipcc.ch/site/assets/uploads/2018/03/sroc02-1.pdf

The Greenhouse Effect

Molecules of that absorb specific wavelengths of IR energy experience different fates:

- Some hold that extra energy for a brief time, then re-emit it in all directions as heat.
- Others collide with atmospheric molecules such as N₂ and O₂ and transfer the absorbed energy to those molecules, as heat

Both processes "trap" radiation emitted by the Earth; this trapping of energy heats the lower atmosphere and surface



Masters, Intro. to Environmental Engineering and Science, 3d ed.

See Chapter 3.4 by Dan Kirk-Davidoff, in *Green Chemistry: An Inclusive Approach*, 2018 in Additional Readings for a simple, differential equation description of the GHG effect based on a so-called two layer model.

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

25

How does RF change with concentration?



Masters, Introduction to Environmental Engineering and Science, 1998

Effectiveness of a GHG depends on "saturation" of absorption band.

Highly saturated (most of the outgoing radiation is already absorbed) bands are less sensitive to increases in GHG concentration than partially or non saturated bands.

How does RF change with concentration?



Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

27

How does RF change with concentration?

Table 8.SM.1 | Supplementary for Table 8.3: RF formulae for CO_2 , CH_4 and N_2O .

Gas	RF (in W m⁻²)	$\textbf{Constant}\alpha$
C0 ₂	$\Delta F = \alpha \ln (C / C_0)$	5.35
CH₄	$\Delta F = \alpha \left(\sqrt{M} - \sqrt{M_0} \right) - \left(f(M, N_0) - f(M_0, N_0) \right)$	0.036
N ₂ O	$\Delta F = \alpha \left(\sqrt{N} - \sqrt{N_0} \right) - \left(f(M_0, N) - f(M_0, N_0) \right)$	0.12

Notes:

f (M , N) = 0.47 ln [1+2.01×10⁻⁵ (MN)0.75 + 5.31×10^{-15} M (MN)^{1.52}]

C is CO₂ in ppm.

M is CH₄ in ppb.

N is N_2O in ppb.

The subscript 0 denotes the unperturbed molar fraction for the species being evaluated. However, note that for the CH_4 forcing N_0 should refer to present-day N_2O , and for the N_2O forcing M_0 should refer to present-day CH_4 .

Graphical representation of surface radiative forcing due to CH_4 and N_2O



Copyright © 2019 University of Maryland

This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

Atmospheric Absorption Absorption (%) CO. N₂O₈ Halocarbon Absorption Spectrum Cross-Sections (cm²/molecule x 10⁻¹⁸) CFC-12 HCFC-22 HFC-134a Wavelength (µm)

Absorption vs. Wavelength

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

How does RF change with concentration?

Table 6.2: Simplified expressions for calculation of radiative forcing due to CO_2 , CH_4 , N_2O , and halocarbons. The first row for CO_2 lists an expression with a form similar to IPCC (1990) but with newer values of the constants. The second row for CO_2 is a more complete and updated expression similar in form to that of Shi (1992). The third row expression for CO_2 is from WMO (1999), based in turn on Hansen et al. (1988).

Trace gas	Simplified expression Radiative forcing, $\Delta F~(Wm^{-2})$	Constants		
co ₂	$\Delta F = \alpha \ln(C/C_0)$	α = 5.35		
CH ₄	$\Delta \mathbf{F} = \boldsymbol{\alpha}(\sqrt[4]{\mathbf{M}} - \sqrt[4]{\mathbf{M}}_0) - (\mathbf{f}(\mathbf{M}, \mathbf{N}_0) - \mathbf{f}(\mathbf{M}_0, \mathbf{N}_0))$	α = 0.036		
N ₂ O	$\Delta F = \alpha(\sqrt[4]{N} - \sqrt[4]{N}_0) - (f(M_0, N) - f(M_0, N_0))$	α = 0.12		
CFC-11a	$\Delta F = \alpha (X - X_0)$	α = 0.25		
CFC-12	$\Delta F = \alpha (X - X_0)$	α = 0.32		

 $f(M,N) = 0.47 \ln[1+2.01 \times 10^{-5} (MN)^{0.75}+5.31 \times 10^{-15} M(MN)^{1.52}]$

C is CO2 in ppm

M is CH4 in ppb

N is N_2O in ppb

X is CFC in ppb

The constant in the simplified expression for CO₂ for the first row is based on radiative transfer calculations with three-dimensional climatological meteorological input data (Myhre etal, 1998b). For the second and third rows, constants are derived with radiative transfer calculations using one-dimensional global average meteorological input data from Shi (1992) and Hansen etal. (1988), respectively.

The subscript 0 denotes the unperturbed concentration.

^a The same expression is used for all CFCs and CFC replacements, but with different values for α (i.e., the radiative efficiencies in Table 6.7).

IPCC Third Assessment Report, 2001

Copyright © 2019 University of Maryland

This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

31



RF Due to Tropospheric Aerosols: Direct Effect



Figure 8.8 | Time evolution of RF due to aerosol-radiation interaction and BC on snow and ice.



Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

33

RF Due to Tropospheric Aerosols: Indirect Effect

Indirect Effects of Aerosols on Clouds

Anthropogenic aerosols lead to more cloud condensation nuclei (CCN) Resulting cloud particles consist of smaller droplets, promoted by more sites (CCN) for cloud nucleation

The cloud that is formed is therefore brighter (reflects more sunlight) <u>and</u> has less efficient precipitation, i.e. is longer lived) ⇒



Large uncertainty in aerosol RF

Fig 2-10, IPCC 2007

- scatter and absorb radiation (direct radiative forcing)
- affect cloud formation (indirect radiative forcing)

Tropospheric Aerosol RF



 ΔRF_{2011} GHGs ≈ 3.2 W m⁻² \Rightarrow climate change is complex but this quantity is <u>well known</u>

 ΔRF_{2011} Aerosols: best estimate is -0.9 W m⁻², probably between -0.4 W m⁻² and -1.5 W m⁻²; could be between -0.1 W m⁻² and -1.9 W m⁻²

Large uncertainty in aerosol RF

- scatter and absorb radiation (direct radiative forcing)
- affect cloud formation (indirect radiative forcing)

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

35



Tropospheric Sulfate Aerosols



Remote sites (blue), Europe (green), & United States (red).

Koch et al., JGR, 2007 https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2005JD007024

Tropospheric Sulfate Aerosols





Koch *et al., JGR,* 2007 https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2005JD007024

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

37

Black Carbon Aerosols

Simulated Black Carbon Aerosol Absorption Optical Depth (AAOD) at 900 nm for year 2007



Wang et al., *JGR*, 2016 https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/2015JD024326

Black Carbon Aerosols

Bond et al., Bounding the role of black carbon in the climate system: A scientific assessment, JGR, 2013 Global climate forcing of black carbon and co-emitted species in the industrial era (1750 - 2005)



	Total Climate Forcing, Black Carbon Aerosols (W m ⁻²)					
Report	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)		
Δ RF, BC	0.1 (0.03 to 0.3)	0.2 (0.1 to 0.4)	0.2 (0.05 to 0.35)	0.4 (0.05 to 0.80)		

Global View

Copyright © 2019 University of Maryland

This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

-2.25

90W

0.15

0.3

2.25

1.5



Greenhouse gases

Organic and black carbon from fossil fuel burning

-0.75



https://www.ipcc.ch/report/ar3/wg1/chapter-6-radiative-forcing-of-climate-change/

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch 39

0.3

0.15

0.45

Combining RF GHGs & Aerosols



Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

41

Combining RF GHGs & Aerosols



Fig 1.10, Paris, Beacon of Hope

Copyright © 2019 University of Maryland

Combining RF GHGs & Aerosols



Copyright © 2019 University of Maryland Fig 1.10, Paris, Beacon of Hope

This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

43

Combining RF GHGs & Aerosols



Fig 1.10, Paris, Beacon of Hope

Copyright © 2019 University of Maryland

Empirical Model of Global Climate (EM-GC)



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

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch





We assume that whatever value of climate feedback is inferred from the climate record will persist into the future. For Aerosol RF in 2011 of –1.5 W m⁻² & assuming best estimate for H₂O and Lapse Rate feedback is correct, this simulation implies sum of <u>other feedbacks</u> (clouds, surface albedo) must be **strongly positive**.



We assume that whatever value of climate feedback is inferred from the climate record will persist into the future. For Aerosol RF in 2011 of -0.9 W m⁻² & assuming best estimate for H₂O and Lapse Rate feedback is correct, this simulation implies sum of <u>other feedbacks</u> (clouds, surface albedo) must be *slightly positive*.

Copyright © 2019 University of Maryland This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch

47



We assume that whatever value of climate feedback is inferred from the climate record will persist into the future. For Aerosol RF in 2011 of -0.4 W m⁻² & assuming best estimate for H₂O and Lapse Rate feedback is correct, this simulation implies sum of <u>other feedbacks</u> (clouds, surface albedo) must be *negative*.