

1.84/10.817/12.807: Atmospheric Chemistry

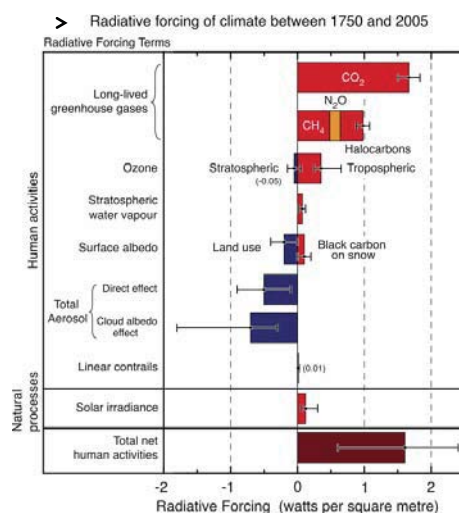
Prof. Jesse Kroll

Today:

- 1) Motivation/Introduction
- 2) Course overview/outline
- 3) Atmosphere, chemistry basics

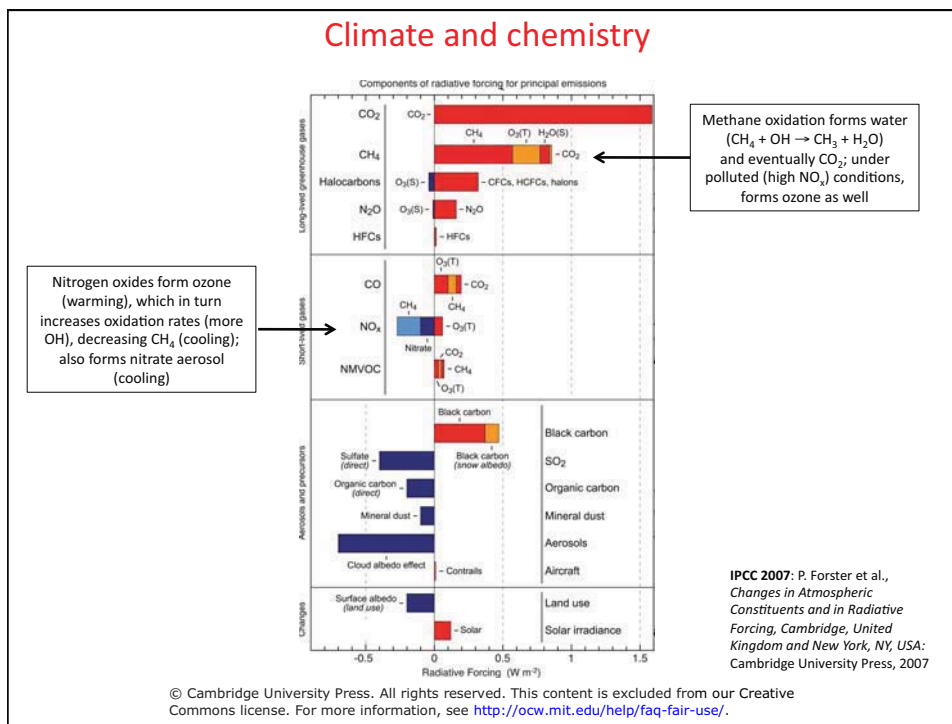
Climate and chemistry

Change in net irradiance (incoming minus outgoing radiation) since 1750



IPCC 2007: P. Forster et al.,
*Changes in Atmospheric
Constituents and in Radiative
Forcing*, Cambridge, United
Kingdom and New York, NY, USA:
Cambridge University Press, 2007

© Cambridge University Press. All rights reserved. This content is excluded from our Creative Commons license. For more information, see <http://ocw.mit.edu/help/faq-fair-use/>.



Ozone depletion

Nature Vol. 249 June 28 1974

Stratospheric sink for chlorofluoromethanes : chlorine atom-catalysed destruction of ozone

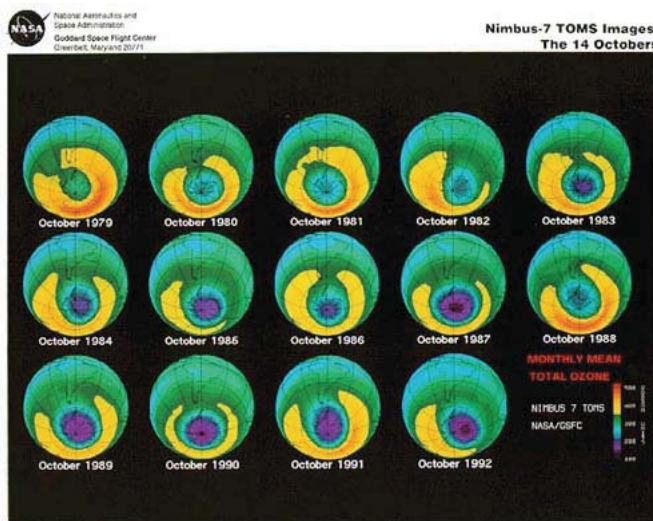
Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

Reprinted by permission from Macmillan Publishers Ltd: Nature.
Source: Nature 249: 810 - 812. © <1974>.

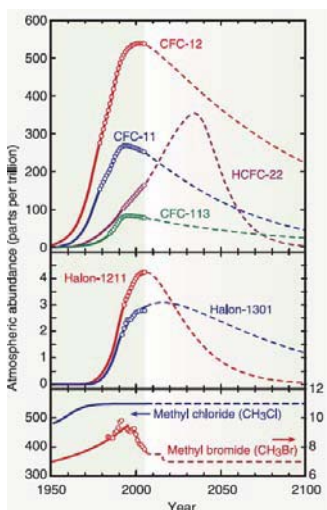
Ozone depletion



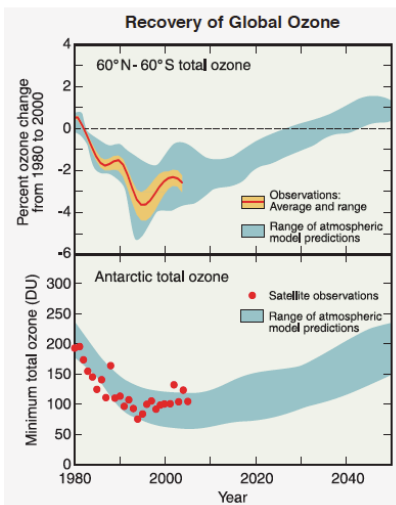
This image is in the public domain.

TOMS (Total Ozone Monitoring Satellite) Data
(global depletion occurring as well)

Ozone depletion: Montreal Protocol



This image is in the public domain.



This image is in the public domain.

WMO/UNEP, *Scientific Assessment of Ozone Depletion: 2006*

Ecological health/biogeochemistry



This image is in the public domain.

acid deposition



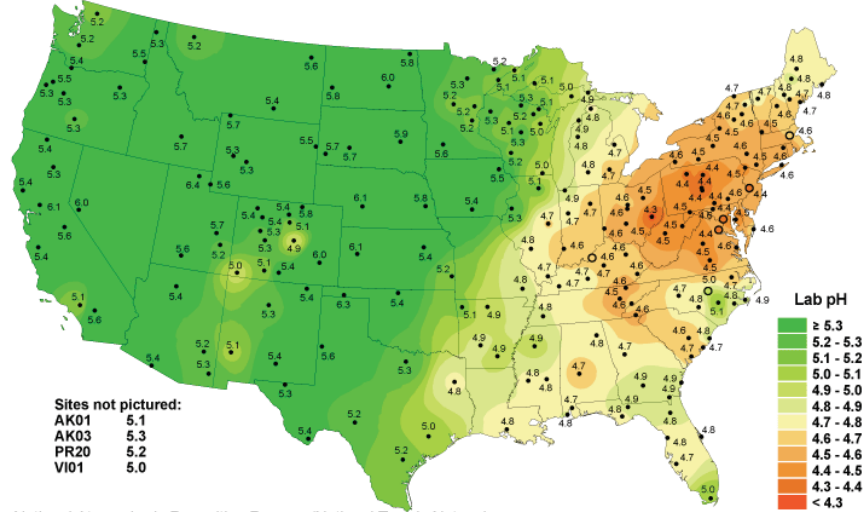
This image is in the public domain.

nutrient deposition

wikipedia

Acid rain

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2007



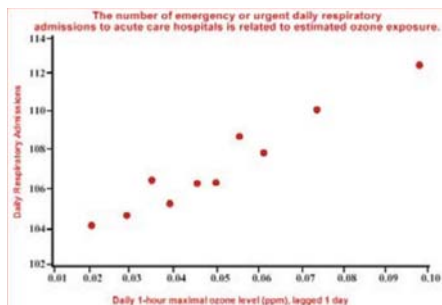
Sites not pictured:
AK01 5.1
AK03 5.3
PR20 5.2
VI01 5.0

National Atmospheric Deposition Program/National Trends Network
<http://nadp.sws.uiuc.edu> This image is in the public domain.

From D. Jacob

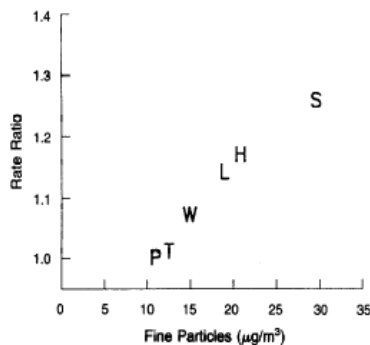
Human health

Ozone



This image is in the public domain.

Particulate matter

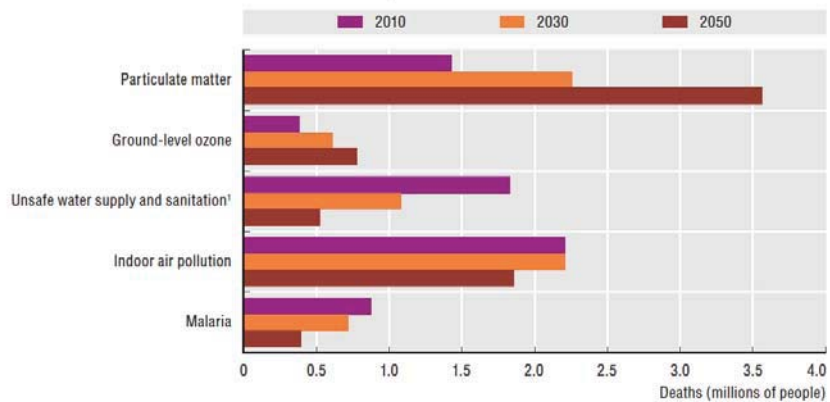


© Massachusetts Medical Society. All rights reserved. This content is excluded from our Creative Commons license. For more information, see <http://ocw.mit.edu/help/faq-fair-use/>.

<http://www.epa.gov/o3healthtraining/population.html>

D. W. Dockery et al., *N. Engl. J. Med.* 329, 1753-1759 (1993)

Air pollution and health, 2010-2050



© Organisation for Economic Co-operation and Development (OECD) (Rights and Permissions Unit). All rights reserved. This content is excluded from our Creative Commons license. For more information, see <http://ocw.mit.edu/help/faq-fair-use/>.

OECD Environmental Outlook to 2050

Visibility

WHO Guideline: 50 µg/m³
averaged over 24 hrs



Images removed removed due to copyright restrictions.

http://news.bbc.co.uk/2/hi/in_pictures/7506925.stm

Key elements in the atmosphere

- abundant
- also important
- less abundant (trace)
- boring

...and many other trace elements

1 IA H 1.01	2 IIA He 4.00																	18 VIIIA Ar 39.95																			
3 IA Li 6.94	4 IIA Be 9.01																	10 VIIIA Ne 20.18																			
11 IIIA Na 22.99	12 IIIA Mg 24.31	13 IIIA B 10.81	14 IVA C 12.01	15 VA N 14.01	16 VIA O 16.00	17 VIIA F 19.00	18 VIIIA Ne 20.18	19 IIIB K 39.10	20 IIIB Ca 40.08	21 IVB Sc 44.96	22 IVB Ti 47.88	23 VB V 50.94	24 VIB Cr 52.00	25 VIIB Mn 54.94	26 VIIB Fe 55.85	27 VIIIB Co 58.93	28 VIIIB Ni 58.69	29 VIIIB Cu 63.55	30 VIIIB Zn 65.39	31 IIIB Ga 69.72	32 IIIB Ge 72.61	33 IVA As 74.92	34 IVA Se 78.96	35 VA Br 79.90	36 VA Kr 83.80												
37 IA Rb 85.47	38 IA Sr 87.62	39 IIA Y 88.91	40 IIA Zr 91.22	41 IIIB Nb 92.91	42 IIIB Mo 95.94	43 IIIB Te 98.91	44 IIIB Ru 101.07	45 IIIB Rh 101.07	46 IIIB Pd 106.42	47 IIIB Ag 107.87	48 IIIB Cd 112.41	49 IIIB In 114.82	50 IIIB Sn 118.71	51 IIIB Sb 121.76	52 IIIB Te 127.6	53 IIIB I 126.9	54 IIIB Xe 131.29	55 IIA Cs 132.9	56 IIA Ba 137.3	57 IIA La* 138.9	58 IIIB Hf 178.5	59 IIIB Ta 180.9	60 IIIB W 183.9	61 IIIB Re 186.2	62 IIIB Os 190.2	63 IIIB Ir 192.2	64 IIIB Pt 195.1	65 IIIB Au 197.0	66 IIIB Hg 200.6	67 IIIB Tl 204.4	68 IIIB Pb 207.2	69 IIIB Bi 209	70 IIIB Po (209)	71 IIIB At (210)	72 IIIB Rn (222)		
87 IIA Fr (223)	88 IIA Ra (226)	89 IIA Ac^A (227)	90 IIIB Rf (261)	91 IIIB Db (262)	92 IIIB Sg (263)	93 IIIB Bh (264)	94 IIIB Hs (265)	95 IIIB Mt (268)	96 IIIB Ds (271)	97 IIIB Rg (272)																											
																		58 IIIB Ce 140.1	59 IIIB Pr 140.9	60 IIIB Nd 144.2	61 IIIB Pm (145)	62 IIIB Sm 150.4	63 IIIB Eu 152.0	64 IIIB Gd 157.3	65 IIIB Tb 158.9	66 IIIB Dy 162.5	67 IIIB Ho 164.9	68 IIIB Er 167.3	69 IIIB Tm 168.9	70 IIIB Yb 173.0	71 IIIB Lu 175.0						
																		90 IIIB Th 232.0	91 IIIB Pa (231)	92 IIIB U 238.0	93 IIIB Np (237)	94 IIIB Pu (244)	95 IIIB Am (243)	96 IIIB Cm (247)	97 IIIB Bk (247)	98 IIIB Cf (251)	99 IIIB Es (252)	100 IIIB Fm (257)	101 IIIB Md (258)	102 IIIB No (259)	103 IIIB Lr (260)						

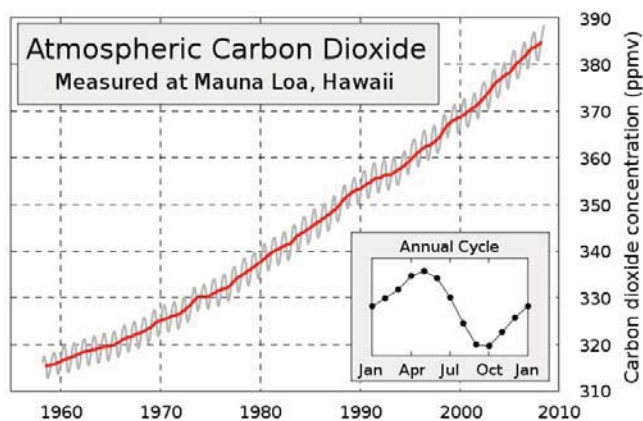
Chemical composition of atmosphere

<i>Chemical Species</i>	<i>Volume fraction, ppm</i>
Nitrogen (N ₂)	780,840 (78.084%)
Oxygen (O ₂)	209,460 (20.946%)
Argon (Ar)	9,340 (0.9340%)
→ Carbon dioxide (CO ₂)	390 (0.039%)
Neon (Ne)	1 .18 (0.001818%)
Helium (He)	5.24 (0.000524%)
→ Methane (CH ₄)	1.79 (0.000179%)
Krypton (Kr)	1.14 (0.000114%)
Hydrogen (H ₂)	0.55 (0.000055%)
→ Nitrous oxide (N ₂ O)	0.3 (0.00003%)
→ Carbon monoxide (CO)	0.1 (0.00001%)
Xenon (Xe)	0.09 (0.000009%)
→ Ozone (O ₃)	0.0 to 0.07 (0 to 0.000007%)
→ Nitrogen dioxide (NO ₂)	0.02 (0.000002%)

Increasing due to human activity

Not included in above dry atmosphere:
Water vapor (H₂O) ~0.40% over full atmosphere,
typically 1%-4% at surface

Atmospheric CO₂



http://en.wikipedia.org/wiki/Keeling_curve

Image courtesy of [Narayanese](#) on Wikimedia. License: CC-BY-SA. This content is excluded from our Creative Commons license. For more information, see <http://ocw.mit.edu/help/faq-fair-use/>.

pre-industrial: ~280 ppm

Chemical composition of atmosphere

Chemical Species	Volume fraction, ppm	Notes on units:
Nitrogen (N ₂)	780,840 (78.084%)	<p>1) ppm, ppb, ppt refer to volume (ppmv, ppbv, etc.)</p> <p>2) For an ideal gas, $PV=nRT$, so <i>volume fraction</i> and <i>mole fraction</i> are the same</p> <p>3) These are <i>mixing ratios</i>, relating amount of the compound to the total amount of air.</p> <p>4) This is different from <i>concentration</i>, which is moles (or molecules) of compound per absolute volume (usually molecules/cm³).</p> <p>5) Can convert between the two, but the conversion depends on P, T (altitude)!</p>
Oxygen (O ₂)	209,460 (20.946%)	
Argon (Ar)	9,340 (0.9340%)	
Carbon dioxide (CO ₂)	390 (0.039%)	
Neon (Ne)	18.18 (0.001818%)	
Helium (He)	5.24 (0.000524%)	
Methane (CH ₄)	1.79 (0.000179%)	
Krypton (Kr)	1.14 (0.000114%)	
Hydrogen (H ₂)	0.55 (0.000055%)	
Nitrous oxide (N ₂ O)	0.3 (0.00003%)	
Carbon monoxide (CO)	0.1 (0.00001%)	
Xenon (Xe)	0.09 (0.000009%)	
Ozone (O ₃)	0.0 to 0.07 (0 to 0.000007%)	
Nitrogen dioxide (NO ₂)	0.02 (0.000002%)	
Not included in above dry atmosphere:		
Water vapor (H ₂ O)	~0.40% over full atmosphere, typically 1%-4% at surface	

“Standard” conditions for temperature and pressure

Temperature	Absolute pressure	Relative humidity	Publishing or establishing entity
°C	kPa	% RH	
0	100.000		IUPAC (present definition) ^[1]
0	101.325		IUPAC (former definition) ^[1] , NIST ^[6] , ISO 10780 ^[7]
15	101.325	0 ^{[8][9]}	ICAO's ISA, ^[8] ISO 13443, ^[9] EEA, ^[10] EGIA ^[11]
20	101.325		EPA, ^[12] NIST ^[13]
25	101.325		EPA ^[14]
25	100.000		SATP ^[15]
20	100.000	0	CAGI ^[16]
15	100.000		SPE ^[17]
20	101.3	50	ISO 5011 ^[18]
°F	psi	% RH	
60	14.696		SPE, ^[17] U.S. OSHA, ^[19] SCAQMD ^[20]
60	14.73		EGIA, ^[11] OPEC, ^[21] U.S. EIA ^[22]
59	14.503	78	U.S. Army Standard Metro ^{[23][24]}
59	14.696	60	ISO 2314, ISO 3977-2 ^[25]
°F	in Hg	% RH	
70	29.92	0	AMCA, ^{[26][27]} air density = 0.075 lbm/ft ³ . This AMCA standard applies only to air.

Courtesy of [Wikipedia](#). License: CC-BY-SA. This content is excluded from our Creative Commons license. For more information, see <http://ocw.mit.edu/help/faq-fair-use/>.

From http://en.wikipedia.org/wiki/Standard_conditions_for_temperature_and_pressure

Oxidizing atmosphere

Oxygen has been called the “ultimate oxidant”¹
 Accepts electrons readily (oxidation state goes down)

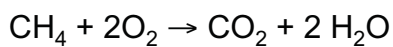
Organic matter is the “ultimate reductant”¹
 Donates electrons readily (oxidation state goes up)

→ Organic carbon will be oxidized in the atmosphere
 (ultimately end-product is CO₂)

(...as will most other elements)

¹ Morel and Hering, *Principles and Applications of Aquatic Chemistry* (Wiley, 1993)

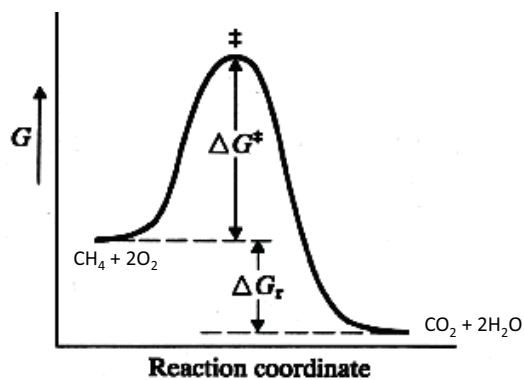
Oxidation: Thermodynamics



molecule	ΔH_f^0 (kJ/mol)	S^0 (J/mol/K)
CH ₄	-74.8	186.2
H ₂ O	-241.8	188.7
CO ₂	-393.5	213.6
O ₂	0.0	205.0

Thermodynamics vs. Kinetics

Spontaneity of a reaction (thermodynamic favorability) tells us **almost nothing** about the rate of a reaction (kinetic favorability)!



© source unknown. All rights reserved. This content is excluded from our Creative Commons license. For more information, see <http://ocw.mit.edu/help/faq-fair-use/>.

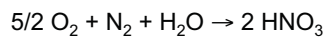


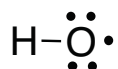
Image removed due to copyright restrictions.
See the book cover of Lewis, G. N., and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances* for further details.

“We see from the large negative free energy of formation of nitric acid that it should be producible directly from its elements. Even starting with water and air, we see by our equation that nitric acid should form until it reaches a concentration of about 0.1 M where the calculated equilibrium exists. **It is to be hoped that nature will not discover a catalyst for this reaction, which would permit all the oxygen and part of the nitrogen of the air to turn the oceans into dilute nitric acid.**”

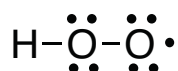
Free radicals

Chemical species that have an unpaired electron (unfilled outer shell)

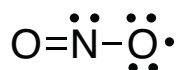
→ Very reactive, and drive most of atmospheric chemistry



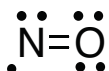
Hydroxyl radical (OH)



Hydroperoxy radical (HO₂)



Nitrogen dioxide (NO₂)

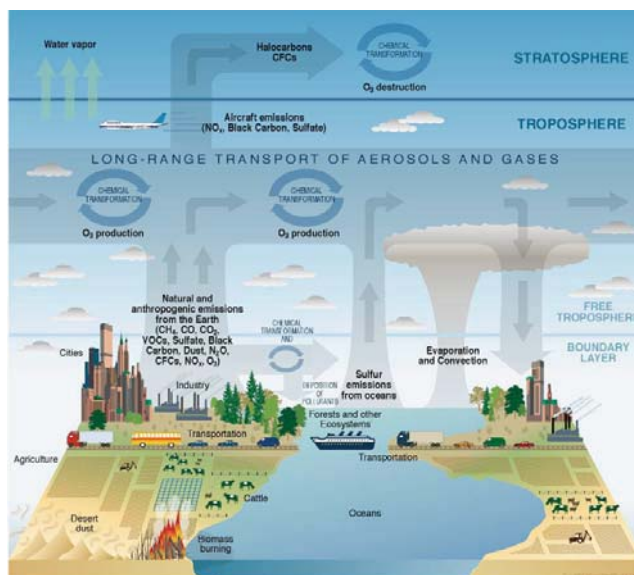


Nitrogen oxide (NO)

What's next

September	4	W	Introduction; atmospheric composition	1-38	
	9	M	Chemical kinetics 1: Reaction rates	75-93	
	11	W	Chemical kinetics 2: Reaction mechanisms	"	
	16	M	Photochemistry and spectroscopy 1	98-135	
	18	W	Photochemistry and spectroscopy 2	"	
	23	M	Temperature, pressure, radiance	720-734	PSet 1

Chemistry of the atmosphere



This image is in the public domain.

Strategic Plan for the U.S. Climate Change Science Program, 2006

MIT OpenCourseWare
<http://ocw.mit.edu>

1.84J / 10.817J / 12.807J Atmospheric Chemistry
Fall 2013

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.