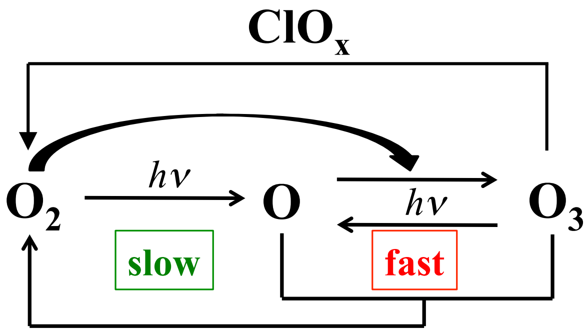
Stratospheric Ozone Layer

- General considerations on the atmosphere
- Fundamentals of chemical kinetics
- Chemistry of the stratospheric ozone layer



ClO_x

O_2 $\xrightarrow{h\nu}$ O $\rightleftarrows$ O_3 ($h\nu$)

slow

fast

Chemical Composition of the Atmosphere

Chemical composition of dry air

Species	Symbol	Molar fraction
Nitrogen	N_2	78 %
Oxygen	O_2	21 %
Argon	Ar	0.93 %
Carbon dioxide	CO_2	0.04 %
Ozone	O_3	1 ppb to 10 ppm
Methane	CH_4	1.8 ppm
Nitrous oxide	N_2O	330 ppb

1 ppm = 10^{-6} mole/mole of air; 1 ppb = 10^{-9} mole/mole of air

Different Phases in the Atmosphere

- Gases
  - Main gases (N_2, O_2)
  - Trace gases (pollutants)
- Liquid water
  - Cloud and fog droplets
  - Raindrops
- Solid water
  - Ice
  - Snow
- Particles
  - Solid
  - Liquid

Radiative Transfer in the Atmosphere

Radiative transfer in the atmosphere depends on the chemical composition of the atmosphere:

- Oxygen and ozone absorb ultraviolet solar radiation in the stratosphere.
- Greenhouse gases (water, carbon dioxide, methane, ozone, nitrous oxide…) absorb infrared terrestrial radiation in the troposphere.
- These processes lead to increases in atmospheric temperature.

Ideal Gas Law

Ideal gas law:

$$P\,V = n\,R\,T$$

P (atm): Atmospheric pressure
V (m^3): Volume of air
T (K): Temperature
$R = 8.31$ J K^{-1} $mole^{-1}$ = 8.2×10^{-5} atm m^3 K^{-1} $mole^{-1}$: Ideal gas law constant
n (moles): number of moles

At $P = 1$ atm and $T = 298$ K (25 ° C): $n / V = 40.9$ moles / m^3

$N = 6.02 \times 10^{23}$ molecules per mole ; 1 atm = 2.46×10^{25} molec m^{-3}

Unit Conversions

1 atm = 2.46×10^{25} molecules m^{-3} = 40.9 moles / m^3

At P = 1 atm:
1 ppb = 10^{-9} atm = 2.46×10^{10} molecules cm^{-3} (ppb: parts per billion)

Conversion of μg/m^3 to ppb
(MW is the molar weight of the chemical species in g/mole):

1 μg/m^3 = $1O^{-6}$ / MW mole/m^3 = $1O^{-6}$/ (40.9 MW) atm = 10^3 / (40.9 MW) ppb

1 ppb = (40.9 MW) / 10^3 μg/m^3

For example, for ozone (MW = 48 g/mole): 1 ppb = 2 μg/m^3

Importance of Atmospheric Ozone

- Radiative properties in the stratosphere: Problem of the destruction of the stratospheric ozone layer
- Air pollutant in the lower atmosphere (troposphere): adverse health effects (pulmonary irritant) and damage to vegetation
- Greenhouse gas
- Ozone is a precursor of the hydroxyl radical, OH, which is the main oxidant in the atmosphere

Chemical Kinetics

The order of a chemical reaction is defined by the number of chemical species that react:

- Monomolecular reactions:
  - Photolytic dissociation (due to solar radiation)

    $A + h\nu \Rightarrow B + C$
  - Thermal dissociation (due to temperature)

    $A \Rightarrow B + C$

- Bimolecular reactions:

  $A + B \Rightarrow C + D$

- Termolecular reactions:

  $A + B + M \Rightarrow C$ where M is O_2 or N_2

Chemical Kinetics

The order of a chemical reaction is defined by the number of chemical species that react:

- Unimolecular reactions:
  - Photolytic dissociation (due to solar radiation)

    $O_3 + h\nu \Rightarrow O_2 + O(^1D)$
  - Thermal dissociation (due to temperature)

    $CH_3C(O)O_2NO_2 \Rightarrow CH_3C(O)O_2 + NO_2$

- Bimolecular reactions:

  $NO + O_3 \Rightarrow NO_2 + O_2$

- Termolecular reactions:

  $NO + NO + O_2 \Rightarrow 2\ NO_2$

Chemical Kinetics

- Elementary reactions: a reaction that actually occurs (i.e., not the representation of a group of reactions)

- Principle of microreversibility: all elementary reactions are reversible.

$$A + B \Rightarrow C + D$$

$$C + D \Rightarrow A + B$$

Therefore: $A + B \Leftrightarrow C + D$

- In most cases, one of the two kinetics prevails and one sees only an irreversible reaction.

Chemical Kinetics

- The reaction rate “constant” characterizes the speed (kinetics) at which the reaction occurs.

- The maximum kinetics is defined by the diffusion of molecules in the host medium (air, water…): it is 4.3×10^{-10} molec^{-1} cm^{3} s^{-1} for a bimolecular reaction.

- The reaction rate constant is actually a function of temperature.

Chemical Kinetics

- Kinetic expression:

$$k = A_T\, T^{B_T} \exp(- E_a / (R\, T))$$

The reaction rate constant is defined by a pre-exponential factor (A_T), the exponent (B_T) of the temperature, and the activation energy (E_a); R is the ideal gas law constant (8.3 J K^{-1} $mole^{-1}$) and T is the temperature in K.

If T^{B_T} shows little variation with temperature compared to the exponential term, then the expression becomes the well-known Arrhenius equation:

$$k = A_T \exp(- E_a / (R\, T))$$

The activation energy represents the energy needed for the reaction to take place. If this energy is very low, $E_a << RT$, i.e. $E_a << 1$ kcal, then $k \sim A_T\, T^{B_T}$

Chemical Kinetics

- Reversible reaction

– If the rate constants of a direct reaction (k_d) and its reverse reaction (k_r) are of the same order of magnitude, one will see a reversible reaction:

$$\begin{array}{lll} A + B & \Rightarrow \; C + D & \qquad k_d \\ C + D & \Rightarrow \; A + B & \qquad k_r \end{array}$$

$$A + B \Leftrightarrow C + D$$

$$K = [C]\,[D] \,/\, [A]\,[B] = k_d \,/\, k_r$$

where K is the equilibrium constant and [A] = molar or molecular concentration of species A

Chemical Kinetics

- Reversible reaction

– If the rate constants of a reaction and its reverse reaction are of the same order of magnitude, one will see a reversible reaction:

$$NO_2 + NO_3 \Rightarrow N_2O_5 \qquad k_d$$
$$N_2O_5 \Rightarrow NO_2 + NO_3 \qquad k_r$$

$$NO_2 + NO_3 \Leftrightarrow N_2O_5$$

$$K = [N_2O_5] / [NO_2]\,[NO_3] = k_d / k_r$$

Chemical Kinetics

- Rate of a chemical reaction

The rate of a chemical reaction, v_r, is defined as follows:

$$\alpha\,\mathrm{A} + \beta\,\mathrm{B} \;\Rightarrow\; \gamma\,\mathrm{C} + \delta\,\mathrm{D} \qquad\qquad k$$

where α, β, γ, and δ are stoichiometric coefficients.

$$v_r = k[\mathrm{A}]^{\alpha}\,[\mathrm{B}]^{\beta}$$

$$v_r = -\frac{1}{\alpha}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{1}{\beta}\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = +\frac{1}{\gamma}\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = +\frac{1}{\delta}\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t}$$

where t is time.

Chemical Kinetics

- Rate of a chemical reaction:
  - In most cases, the coefficients are = 1
  - The kinetics of a chemical reaction is then defined as follows:

$$A + B \Rightarrow C + D \qquad k$$

$$v_r = k[A][B]$$

$$v_r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[C]}{dt} = +\frac{d[D]}{dt}$$

Photochemical Reactions

- Absorption of a photon from solar radiation by a molecule

$$AB + h\nu(\lambda) \Rightarrow AB^*$$

AB is a molecule (A and B are atoms or molecules)

λ is the wavelength of the absorbed radiation

ν is the frequency of the absorbed photon

AB* is the excited state of AB

- AB* being unstable, one can have:

- Collision

$AB^* + M \Rightarrow AB + M$ (where M is O_2 or N_2)

- Dissociation reaction (the chemical bond is broken)

$AB^* \Rightarrow A + B$

Photochemical Reactions

- Absorption of a photon from solar radiation by a molecule of oxygen

$$O_2 + h\nu(\lambda) \Rightarrow O_2^*$$

- O_2^* being unstable, one can have:
  - Collision

    $O_2^* + M \Rightarrow O_2 + M$ (where M is O_2 or N_2)
  - Dissociation reaction (the O-O bond is broken)

    $O_2^* \Rightarrow O + O$

Photochemical Reactions

- Absorption of a photon from solar radiation by a molecule

$$AB + h\nu(\lambda) \;\Rightarrow\; AB^* \;\Rightarrow\; A + B^*$$

The energy provided by the photons must be sufficient to break the bond linking the atoms of the molecule:

$$\boxed{\text{Energy of one photon: } h\nu = h\,c/\lambda}$$

where h: Planck constant (6.6×10^{-34} $m^2\,kg\,s^{-1}$) ; $\nu(\lambda)$: frequency of the photon;

λ: wavelength => Energy of one photon: $h\nu = h\,c/\lambda = 5 \times 10^{-19}$ J at 400 nm

Energy of dissociation of the oxygen bond $\approx$ 500 kJ/mole = 8.3×10^{-19} J/molec

Therefore, visible light ($\lambda > 400$ nm) does not have enough energy to break O_2; the photolysis of O_2 occurs for $\lambda < 242$ nm

Atomic Oxygen

- Different states of atomic oxygen:
  - Triplet state: $O(^3P)$
  - Singlet state: $O(^1D)$ (more excited and unstable)

$$O_2 + h\nu \Rightarrow O(^3P) + O(^3P)$$

$$O_3 + h\nu \Rightarrow O_2 + O(^1D)$$

- Stabilization of $O(^1D)$ by collision with air molecules (O_2 and N_2) represented by M:

$$O(^1D) + M \Rightarrow O(^3P) + M$$

- Everywhere hereafter: O is used for $O(^3P)$

Photolytic Rate Constant

- Rate constant for photolysis at wavelength λ:

$$\boxed{J = \sigma_J(\lambda)\ I_J(\lambda)\ \phi_J(\lambda)}$$

where σ_{AB} = absorptive properties of the molecule AB = effective cross-section of the absorption of radiation at the wavelength λ (cm^2 $molecule^{-1}$)

$I_j(\lambda)$ = radiation received = actinic flux in photons cm^{-2} s^{-1}

$\phi_j(\lambda)$ = quantum yield = fraction of AB that participates in the reaction (molecule/photon)

Photolytic Rate Constant

- $J = 0$ at night because only solar radiation is strong enough for photolysis to occur:

$$\phi_j(\lambda) \approx 0 \text{ for } \lambda > 730 \text{ nm (i.e., in the infrared)}$$

Radiation received, $I_j(\lambda)$ depends on:

- the solar zenith angle (angle of solar radiation with the vertical direction): function of hour, day, longitude, and latitude
- atmospheric conditions (presence of aerosols, haze, clouds…)
- altitude

Daytime Chemistry and Nighttime Chemistry

- Daytime chemistry:
  - Photolysis => atoms and radicals => high reactivity of the atmosphere

- Nighttime chemistry
  - No photolysis => few radicals => low reactivity of the atmosphere

Stratosphere and Troposphere

- Stratosphere :
  - O_2 and O_3 absorb ultraviolet solar radiation ($\lambda < 400$ nm)
  - Source of atomic oxygen to form O_3:

    $O_2 + h\nu \Rightarrow O + O \qquad \lambda < 242$ nm

- Troposphere
  - Solar radiation, which is effective for photolysis, is in the range:

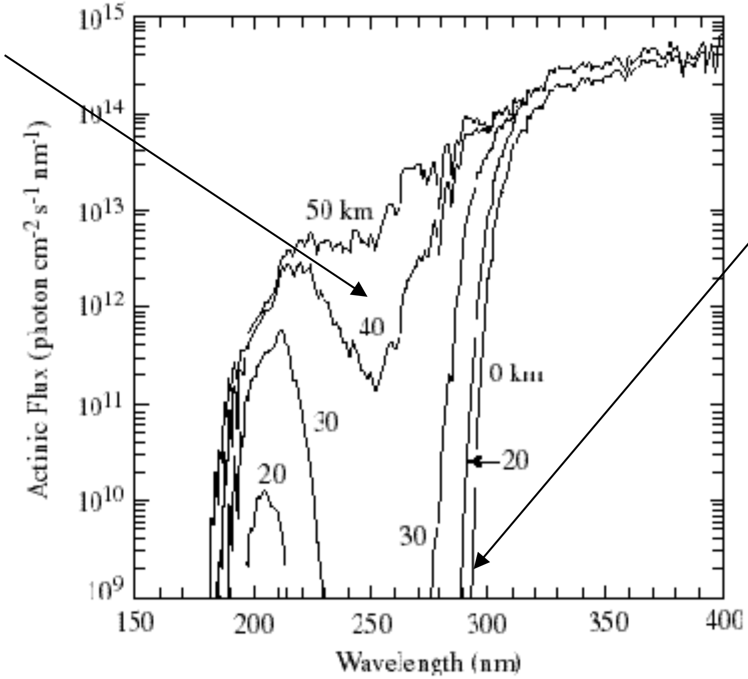
    $290 \text{ nm} < \lambda < 730$ nm
  - Source of atomic oxygen to form O_3:

    $NO_2 + h\nu \Rightarrow NO + O \qquad 300 < \lambda < 420$ nm

Stratosphere and Troposphere

Stratosphere

Troposphere
(< 15 km)



Actinic flux as a function of wavelength
at different altitudes in the atmosphere

Source: DeMore et al., 1997

Oxidizing Power of the Atmosphere

- Production of OH
  - Ozone photolysis leads to OH production:

$$O_3 + h\nu\ (\lambda < 310\ \text{nm}) \Rightarrow O_2 + O(^1D)$$

The excited oxygen atom becomes stable by reaction:

$$O(^1D) + M \Rightarrow O(^3P) + M$$

$$O(^1D) + H_2O \Rightarrow 2\ OH$$

Stratospheric Chemistry of Ozone

- The stratospheric ozone layer plays a protective role against ultraviolet (UV) radiation.
- The absorption of solar radiation leads to an increase of temperature in the stratosphere => stable conditions.
- There is little mass transfer between the stratosphere and the troposphere because of this stable condition at the tropopause (the boundary between the stratosphere and the troposphere).
- The tropopause can be defined by the change in the temperature vertical profile (heat transfer definition), by the change in the potential vorticity (dynamic definition) or by the change in the ozone concentration (chemical definition).

Stratospheric Chemistry of Ozone
History

- Sidney Chapman (1888-1970) proposed in 1930 a cycle of reactions to explain the high concentrations of ozone in the stratosphere (Chapman, S. On ozone and atomic oxygen in the upper atmosphere ; *Phil. Mag*. S. 7, **10**, 369-383, 1930).

- A comparison of his calculations with measurements showed a slight overestimation: the chemical mechanism was then improved in the 1950s with reactions involving OH and HO_2 radicals.

Chapman Cycle

- Oxygen photolysis (slow)

  $O_2 + h\nu \ (\lambda < 240 \text{ nm}) \Rightarrow O + O$ $\qquad k_1$

- Ozone production (fast)

  $O + O_2 + M \Rightarrow O_3 + M$ $\qquad k_2$

- Ozone photolysis (fast)

  $O_3 + h\nu \ (240 < \lambda < 320 \text{ nm}) \Rightarrow O_2 + O(^1D)$ $\qquad k_3$

- Ozone destruction (slow)

  $O + O_3 \Rightarrow 2\,O_2$ $\qquad k_4$

Ozonolysis

- Ozone photolysis

  $O_3 + h\nu \ (240 < \lambda < 320 \text{ nm}) \Rightarrow O_2 + O(^1D)$

- Ozone production

  $O(^1D) + M \Rightarrow O$

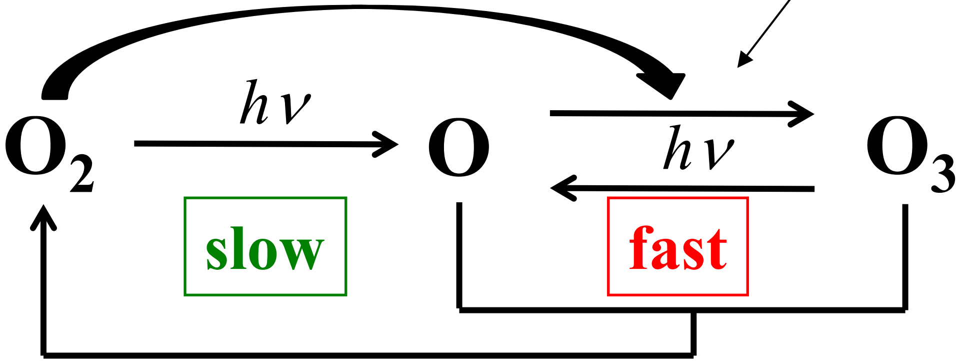
  $O + O_2 + M \Rightarrow O_3 + M$

- Net chemical budget: zero (production = destruction)

- Heat budget: solar radiation => heat (increase in temperature)

Chapman Cycle

Characteristic time < 100 s



O_2 $\xrightarrow{h\nu}$ O $\rightleftarrows$ O_3

$h\nu$

slow

fast

Characteristic time
1 day to several years depending on altitude and latitude

Stratospheric Chemistry of Ozone History

- In the 1960s, the increase in air traffic led to an increase in nitrogen oxide emissions (NO_x) at high altitude; a chemical mechanism suggested a possible destruction of ozone due to a catalytic cycle including NO and NO_2 (P. Crutzen, National Center for Atmospheric Research (NCAR); H. Johnston, University of California at Berkeley)

- In the 1970s, the use of chemical compounds (chlorofluorocarbons, CFC), which were relatively inert in the troposphere, but were potentially photolyzed in the stratosphere, was suggested to lead to the destruction of the ozone layer via a catalytic reaction cycle (F.S. Rowland et M. Molina, University of California at Irvine)

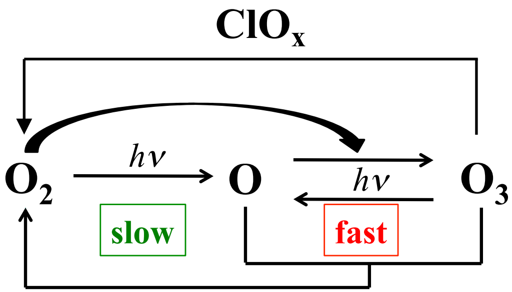
Destruction of O_3 by Catalysis with CFC

Chlorofluorocarbons (CFC) that do not contain a hydrogen atom, are not very reactive in the troposphere and are transported (slowly but surely) to the stratosphere where they can be photolyzed.

Initiation: $CFC + h\nu \Rightarrow Cl + \text{radical } (CFCl_2, CF_2Cl\ldots)$

Propagation: $O_3 + Cl \Rightarrow O_2 + ClO$
$ClO + O(^1D) \Rightarrow O_2 + Cl$

ClO_x
Net budget: $O_3 + O(^1D) \Rightarrow 2\ O_2$

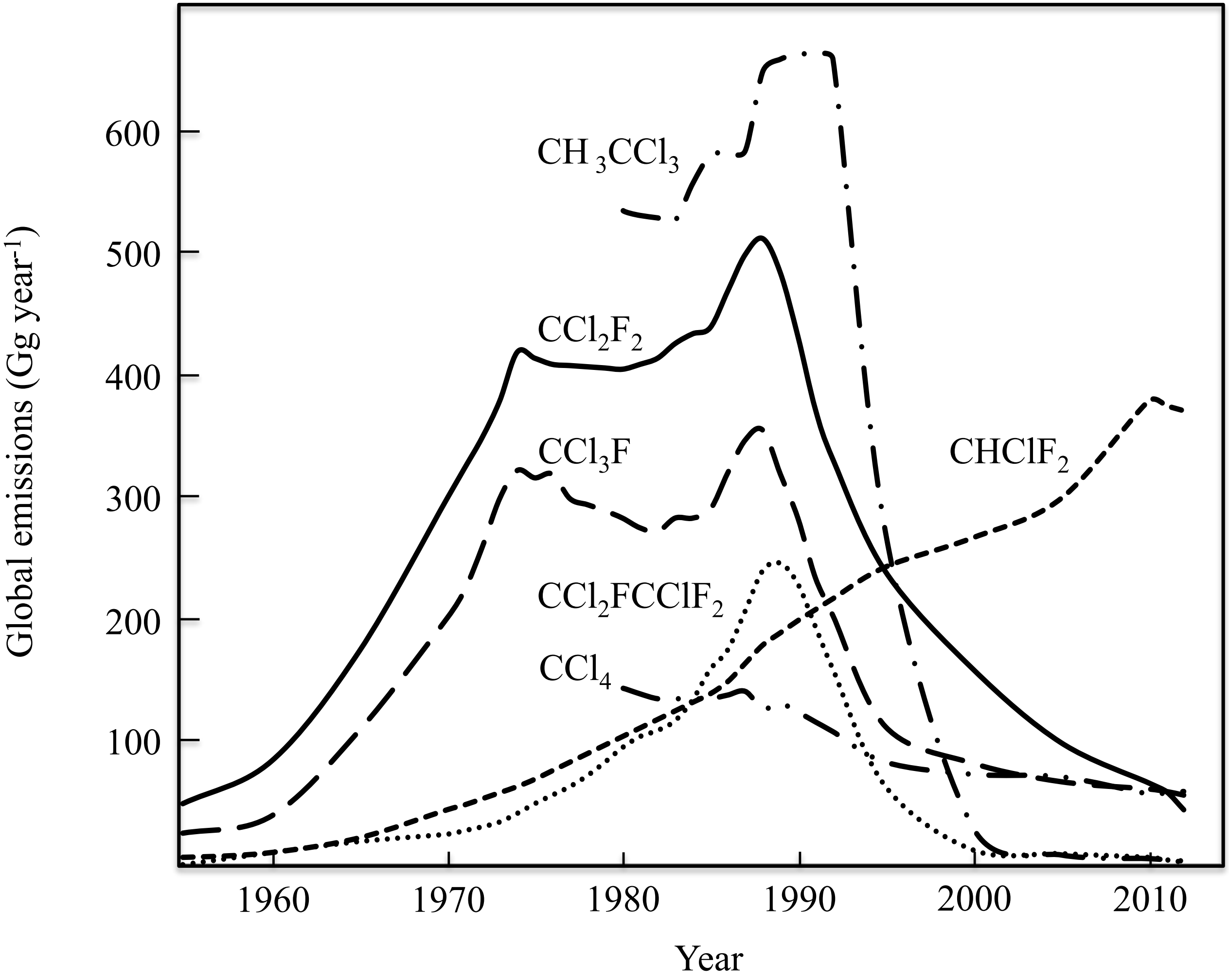


Termination: $Cl + CH_4 \Rightarrow HCl + CH_3$
(for example) $ClO + NO_2 + M \Rightarrow ClNO_3 + M$

Stratospheric Chemistry of Ozone
History

- 1987: The Montreal protocol, which aims to reduce chlorofluorocarbon emissions, is signed by 24 countries and the European Union; it is amended in 1990, 1992, 1995, 1997, 1999, and 2016 (as of 2015, all 197 countries of the United Nations have ratified the protocol and its amendments)
- 1995: Nobel Prize in Chemistry for Paul Crutzen (then at the Max Plack Institute, Germany), F. Sherwood Rowland (University of California at Irvine), and Mario Molina (then at MIT)

Global Emissions of Chlorocarbons



Global Concentrations of Chlorocarbons