Development of Chemical Gas-Phase Mechanisms for Modeling

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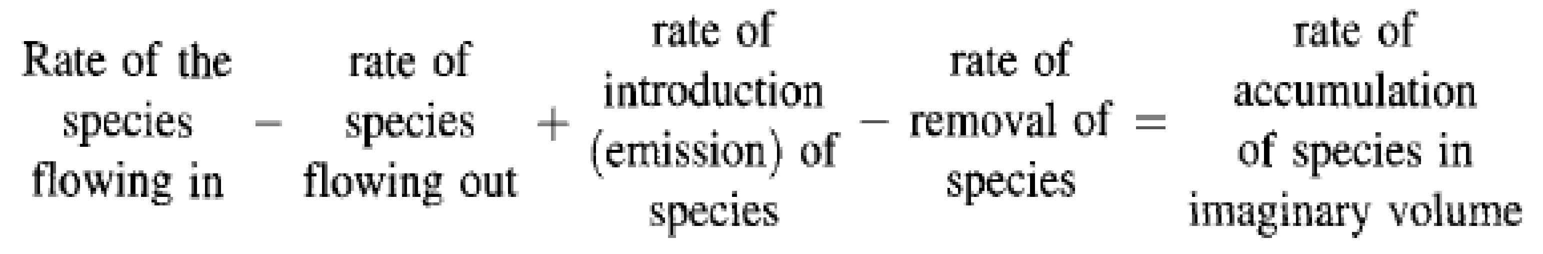
Problem

- While in the air, a substance can be chemically altered in one of two ways.
- First, the sunlight itself may contain sufficient energy to break the molecule apart, a so-called photochemical reaction.
- The more frequently occurring chemical alteration, however, takes place when two molecules interact and undergo a chemical reaction to produce new species.
- Atmospheric chemical transformations can occur homogeneously or heterogeneously.
- Homogeneous reactions occur entirely in one phase;
- Heterogeneous reactions involve more than one phase, such as a gas interacting with a liquid or with a solid surface.
- How to estimate the rate of chemical destruction or production of the gaseous species?

Physical Principles

- The fundamental physical principle governing the behavior of a chemical in the atmosphere is conservation of mass.
- [illegible]



$$\begin{array}{c}\text{Rate of the}\\ \text{species}\\ \text{flowing in}\end{array} - \begin{array}{c}\text{rate of}\\ \text{species}\\ \text{flowing out}\end{array} + \begin{array}{c}\text{rate of}\\ \text{introduction}\\ \text{(emission) of}\\ \text{species}\end{array} - \begin{array}{c}\text{rate of}\\ \text{removal of}\\ \text{species}\end{array} = \begin{array}{c}\text{rate of}\\ \text{accumulation}\\ \text{of species in}\\ \text{imaginary volume}\end{array}$$

- This balance must hold from the smallest volume of air all the way up to the entire atmosphere.

Conservation of Mass

$$\frac{dQ}{dt} = (F_{\text{in}} - F_{\text{out}}) + (P - R)$$

- If we let *Q* denote the total mass of the substance in the volume of air;
- Fi_n and F_{out} the mass flow rates of the substance in and out of the air volume, respectively;
- *P* the rate of introduction of the species from chemical sources;
- and *R* the rate of chemical removal of the species

Steady-State Conditions

$$F_{in} + P = F_{out} + R$$

- If the amount *Q* of the substance in the volume or reservoir is not changing with time, then
- *Q* is a constant and $dQ/dt = 0$. In order for *Q* to be unchanging, all the sources of the substance to the reservoir must be precisely balanced by the sinks of the substance.
- In such a case *steady-state* conditions are said to hold.

REACTION RATES

- A **reaction rate** is the time rate of change of concentration of any reactant in a reaction.
- The rate of an elementary chemical reaction equals a rate coefficient multiplied by the concentration of each reactant.

Reactant Concentration

$$\xi_i = \frac{c_i}{c_{\text{total}}}$$

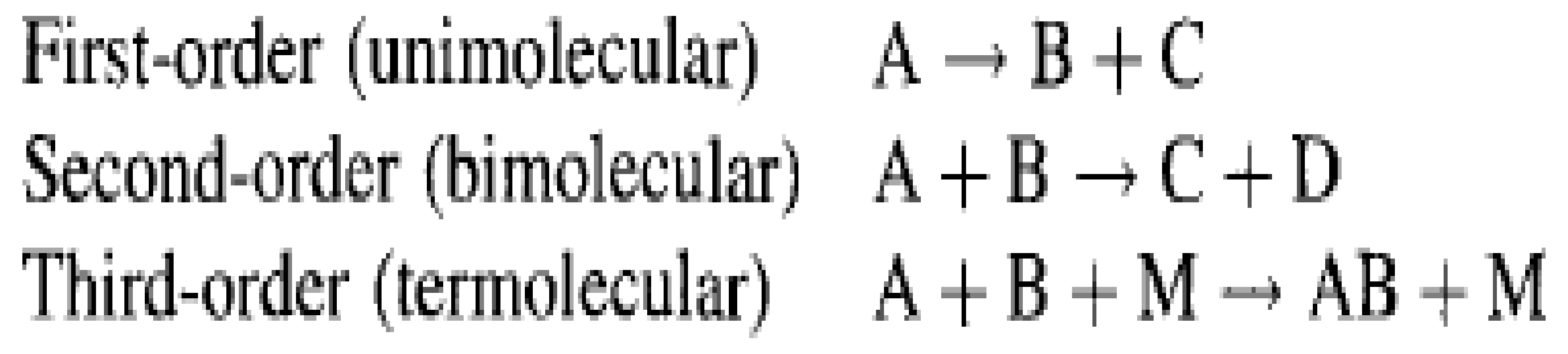
- The SI unit for the amount of a substance is the mole (mol). The number of atoms or molecules in 1 mol is Avogadro's number, *NA =* 6.022 10^{23} mol^{-1}.
- Concentration is the amount (or mass) of a substance in a given volume divided by that volume.
- *Mixing ratio* in atmospheric chemistry is defined as the ratio of the amount (or mass) of the substance in a given volume to the total amount (or mass) of all constituents in that volume.
- In this definition for a gaseous substance the sum of all constituents includes all gaseous substances, including water vapor, but *not* including particulate matter or condensed phase water.
- Thus mixing ratio is just the fraction of the total amount (or mass) contributed by the substance of interest.

Units of Reaction Rate

- If reactant concentrations are expressed in units of molecules of gas per cubic centimeter of air, the rate of reaction is in units of molec cm^{-3} s^{-1}, regardless of whether the reaction has a first-, second-, or third-order rate coefficient;
- A **rate coefficient** relates concentrations to a reaction rate and depends on the reaction order.

ORDER OF REACTION

We consider three types of chemical reaction:



First-order (unimolecular)	$A \rightarrow B + C$
Second-order (bimolecular)	$A + B \rightarrow C + D$
Third-order (termolecular)	$A + B + M \rightarrow AB + M$

Air Concentration

$$[\mathrm{M}] = \mathrm{N_a} = \frac{p_\mathrm{a}}{k_\mathrm{B}T}$$

$$[\mathrm{N_2}] = \chi_{\mathrm{N_2}}\mathrm{N_d} \qquad [\mathrm{O_2}] = \chi_{\mathrm{O_2}}\mathrm{N_d}$$

- The concentration (molecules per cubic centimeter of air) of M is that of total air, and is estimated based on ideal gas law;
- where p_a is total air pressure (hPa), k_B is Boltzmann's constant (1.380658×10^{-19} $\mathrm{cm^3\ hPa\ K^{-1}\ molec.^{-1}}$), and T is absolute temperature (K).
- The concentration of molecular nitrogen and molecular oxygen in the air, often needed to calculate reaction rates;
- where $\chi_{\mathrm{N2}} = 0.7808$ and $\chi_{\mathrm{O2}} = 0.2095$ are the volume mixing ratios of molecular nitrogen and oxygen, respectively

First-order reaction rate

$$A -> B + C$$

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}]$$

$$\frac{dB}{dt} = \frac{dC}{dt} = k_1 A$$

- The rate of a first-order reaction is expressed in molecules cm^{-3} s^{-1}
- the first-order rate coefficient k_1 has units of s^{-1} (reciprocal seconds)

True first-order reactions

$$^{222}\mathrm{Rn} \rightarrow {}^{218}\mathrm{Po} + \alpha\text{-particles}$$

- Few reactions are truly first-order, in that they involve decomposition of a molecule without intervention of a second molecule.
- The classic example of a true first-order reaction is radioactive decay

Photodissociation Reactions

$$\mathrm{A} + h\nu \rightarrow \mathrm{B} + \mathrm{C}$$

$$\frac{dB}{dt} = \frac{dC}{dt} = -\frac{dA}{dt} = J_A A$$

- In the atmosphere, by far the most important class of first-order reactions is photodissociation reactions in which absorption of a photon of light *(hv)* by the molecule induces chemical change;
- *hv* represents a photon of light of frequency v.
- In the photolysis of species A, the rate coefficient is customarily denoted by the symbol j_A

Photodissociation rate parameters depend on spectrally resolved actinic flux.

Photolysis Rate Parameter

$$J = \int I(\lambda) \times \sigma(\lambda) \times \varphi(\lambda)\, d\lambda$$

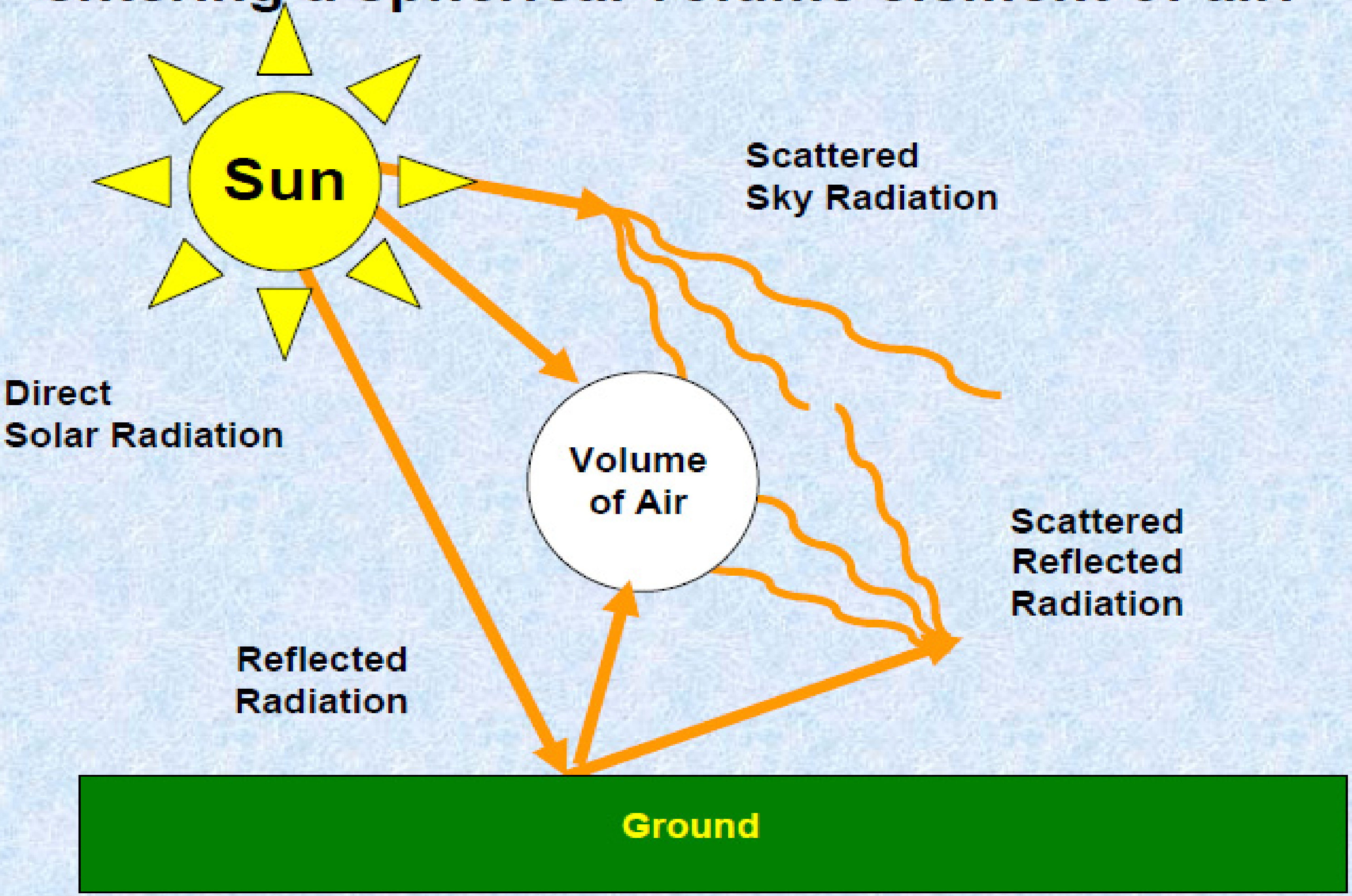
Actinic Flux

Absorption
Cross-Section

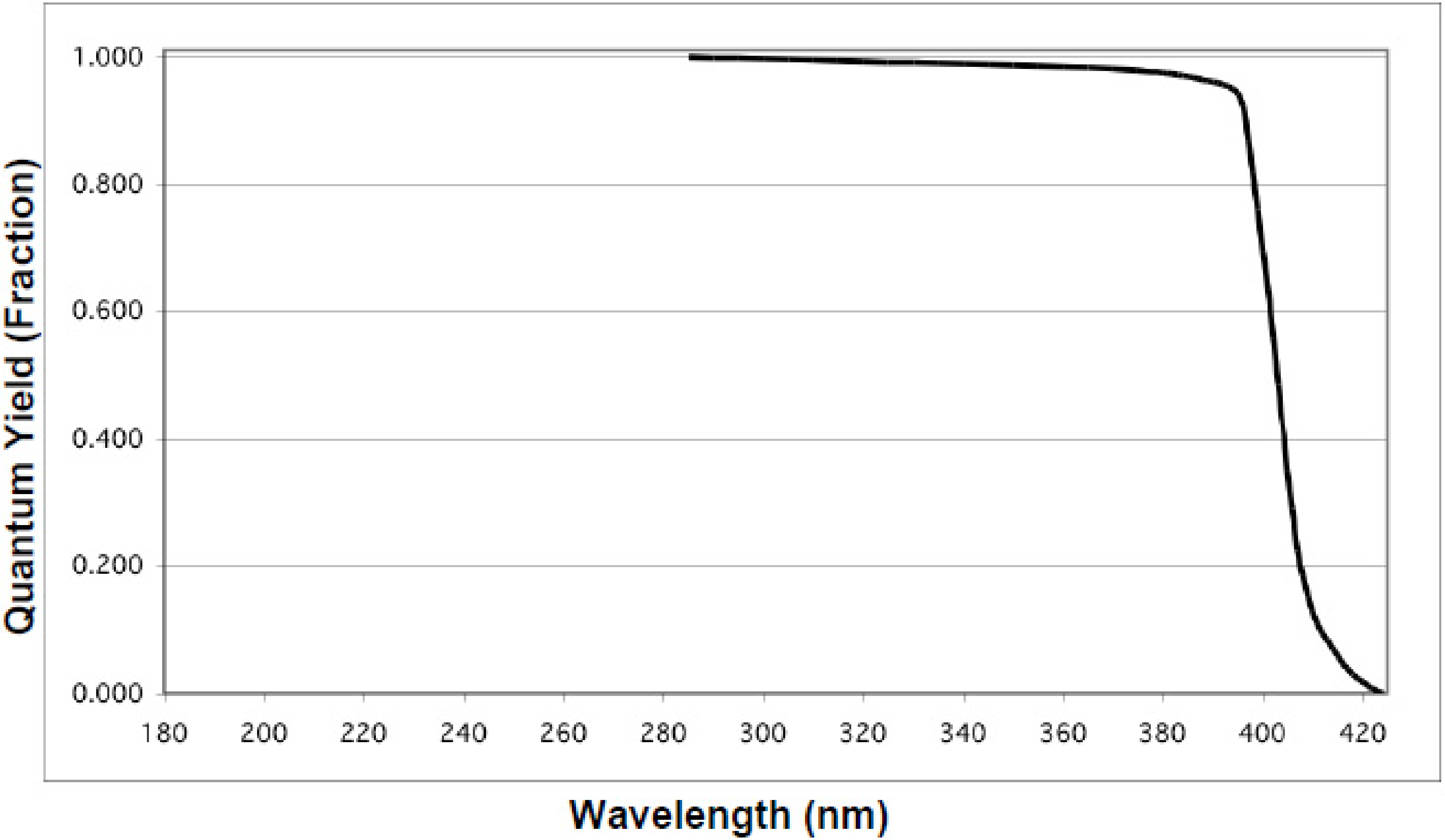
Quantum Yield

Wavelength

Actinic Flux is total flux entering a spherical volume element of air.



QUANTUM YIELD: $NO_2 + h\nu \rightarrow NO + O(^3P)$



Thermal decomposition

$$A + M \rightarrow B + C + M$$

$$\frac{dB}{dt} = \frac{dC}{dt} = -\frac{dA}{dt} = k_T \cdot A \cdot M$$

$$k_1 = k_T \cdot M$$

- Thermal decomposition of a molecule is often represented as first-order, but the energy required for decomposition is usually supplied through collision with another molecule.
- If the other molecule is an air molecule, it is denoted as M

Two Stages of Thermal Decomposition

$$A+M->A^{*}+M, \quad k_A$$

$$A^{*} \rightarrow B+C, \quad k_R$$

OR

$$A^{*}+M \rightarrow A+M, \quad k_D$$

- Apparently unimolecular reaction is really the result of the processes of activation, reaction and deactivation

Rate of two stage reaction

$$-\left(\frac{\mathrm{d(A)}}{\mathrm{dt}}\right) = \mathrm{k_r(A^*)}$$

$$\frac{\mathrm{d(A^*)}}{\mathrm{dt}} = 0 = \mathrm{k_{act}(A)(M)} - [\mathrm{k_d(M)} + \mathrm{k_r}]\,\mathrm{(A^*)}$$

$$\mathrm{(A^*)} = \frac{\mathrm{k_{act}(A)(M)}}{\mathrm{k_r} + \mathrm{k_d(M)}}$$

$$\frac{\mathrm{d(A)}}{\mathrm{dt}} = -\left(\mathrm{k_r}\frac{\mathrm{k_{act}(A)(M)}}{\mathrm{k_r} + \mathrm{k_d(M)}}\right)$$

$$\mathrm{k_u} = \mathrm{k_{act}(M)}\,\frac{\mathrm{k_r}}{\mathrm{k_r} + \mathrm{k_d(M)}}$$

- The rate of decomposition of A (which is equal to the rate of formation of B or C);
- The steady state concentration of $A*$ is derived;
- and the effective first order reaction rate k_u (sec^{-1})

Second-order reactions

$$A + B \rightarrow C + D$$

- The rate of a second-order, or bimolecular, reaction is

$$\frac{d[A]}{dt} = -k_2[A][B]$$

- where the second-order rate coefficient k_2 has units of cm^3 $molecule^{-1}$ s^{-1}.

Collision Theory

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}$$

$$R_{\mathrm{AB}} = -\frac{dn_{\mathrm{A}}}{dt} = -\frac{dn_{\mathrm{B}}}{dt} = \pi d^2 \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2} n_{\mathrm{A}} n_{\mathrm{B}}$$

$$R_{\mathrm{AB}} = \pi d^2 \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2} \exp\left(-\frac{E}{RT}\right) n_{\mathrm{A}} n_{\mathrm{B}}$$

$$k = \underbrace{\pi d^2 \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2}}_{A} \exp\left(-\frac{E}{RT}\right)$$

- Consider the bimolecular reaction
- If reaction occurred with every collision, then the rate of reaction between A and B would be just
- Not every collision will result in reaction; only those collisions that have sufficient kinetic energy to surmount the energy barrier for reaction will lead to reaction. For a Maxwell distribution the fraction of encounters that have energy greater than a barrier *E* (kJ mol-1) is *exp(—E/RT).*
- The rate of reaction is then

Arrhenius form

- As indicated, the terms multiplying the exponential are customarily denoted by *A*, the *collision frequency factor*, or simply the *preexponential factor.*
- Thus, the reaction rate coefficient consists of two components, the frequency with which the reactants collide and the fraction of collisions that have enough energy to overcome the barrier to reaction.
- In many cases the preexponential factor can be considered to be independent of temperature, and the rate coefficient is written as

$$k = A\exp\left(-\frac{E}{RT}\right)$$

Termolecular reactions

$$A + B + M \rightarrow AB + M$$

$$A + B \rightarrow AB^{\dagger}$$

$$AB^{\dagger} + M \rightarrow AB + M$$

$$A + B \xrightarrow{M} AB$$

- The termolecular reaction actually does not take place as the result of the simultaneous collision of all three molecules A, B, and M.
- The probability of such an event happening is practically zero.
- Rather, what actually occurs is that molecules A and B collide to produce an energetic intermediate $AB^{\dagger}$ (the dagger representing vibrational excitation)
- In order for $AB^{\dagger}$ to proceed to the product AB, its excess energy must be removed through collision with another molecule denoted by M, to which the excess energy is transferred

Lifetime

$$\tau = \frac{Q}{R + F_{\mathrm{out}}}$$

- The average residence time or lifetime x, in terms of the quantities introduced earlier
- Calculations of lifetimes can be useful in estimating how far from its source a species is likely to remain airborne before it is removed from the atmosphere.

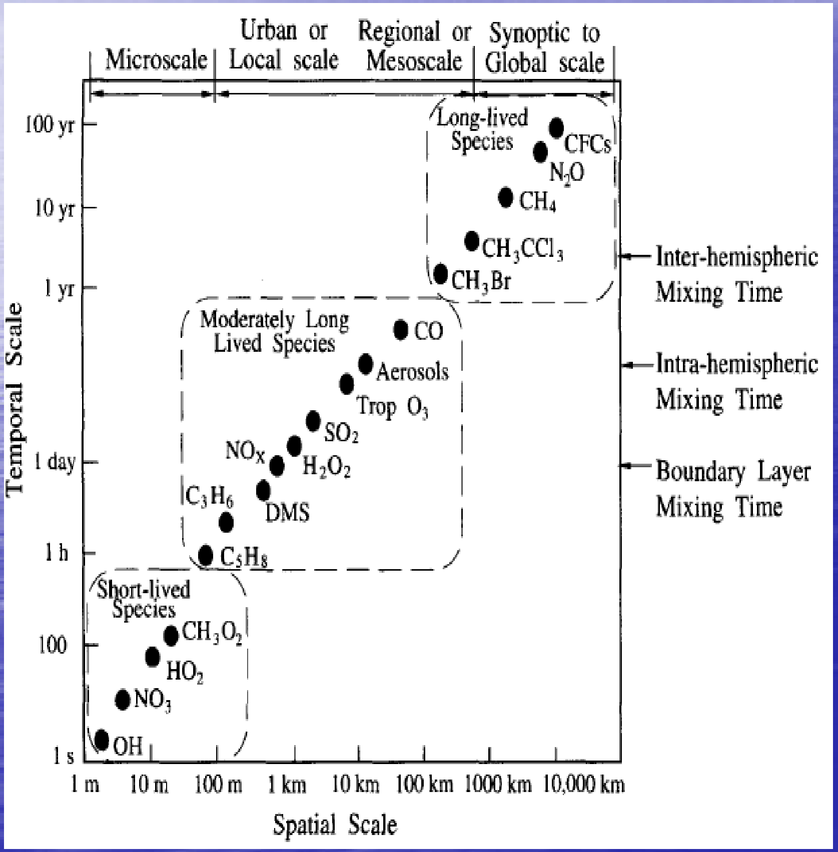
E-folding time of the reaction

$$[A] = [A]_0 \, e^{-k_1 t}$$

$$\tau = 1/k_1$$

- The rate equation can be integrated to give
- Thus, species A decays to *1/e* of its initial concentration in time
- This time is referred to as the e-folding time of the reaction, or the mean lifetime of A against this reaction.

SPATIAL AND TEMPORAL SCALES OF ATMOSPHERIC SPECIES

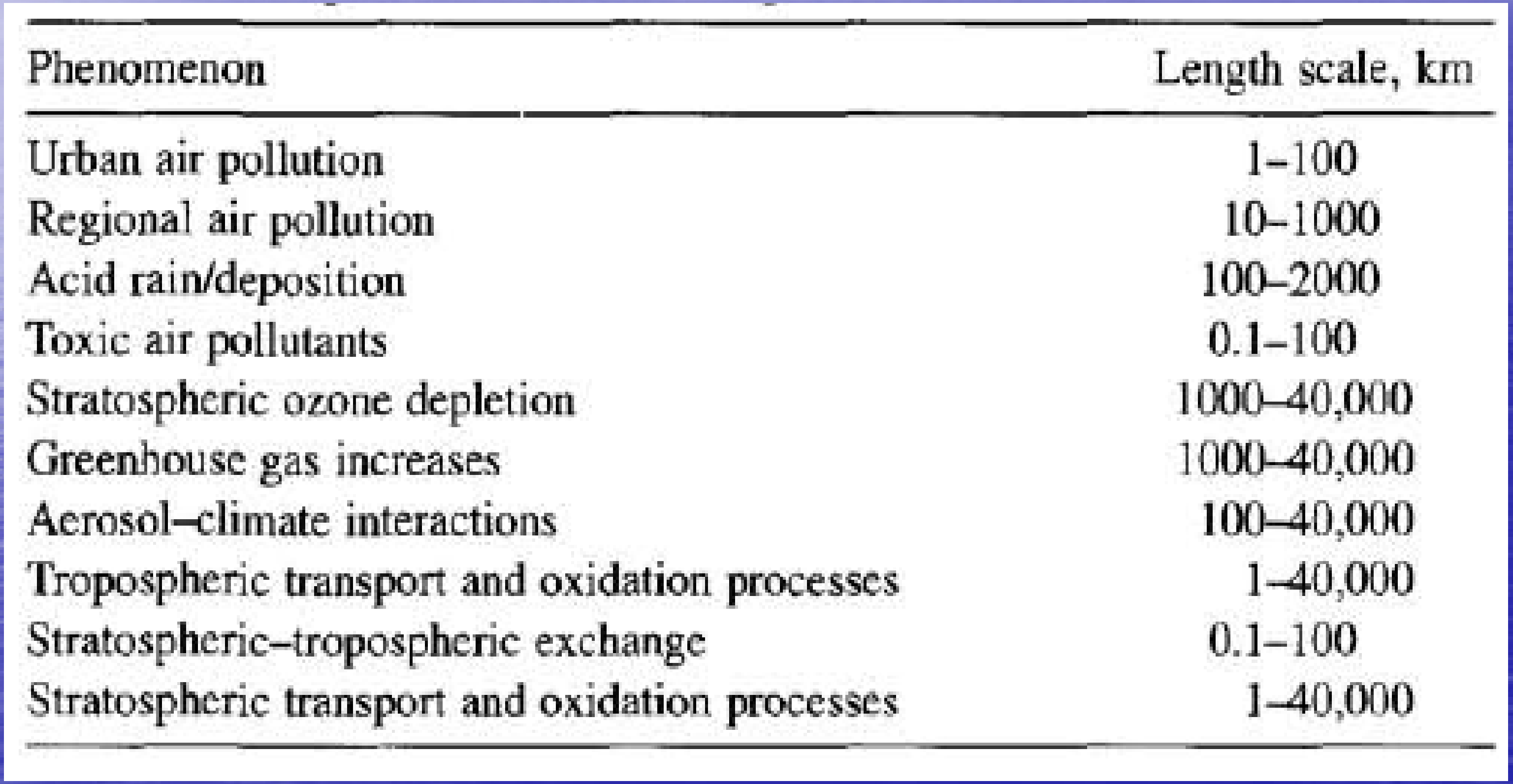


- The verage lifetime of a gas molecule introduced into the atmosphere can range from seconds to millions of years, depending on the effectiveness of the removal processes.
- Most of the species considered air pollutants (in a region in which their concentrations exceed substantially the normal background levels) have natural as well as man-made sources.
- Therefore, in order to assess the effect human-made emissions may have on the atmosphere as a whole, it is essential to understand the atmospheric cycles of the trace gases, including natural and anthropogenic sources as well as predominant removal mechanisms.

Four rough categories have proved convenient to classify atmospheric scales of motion:

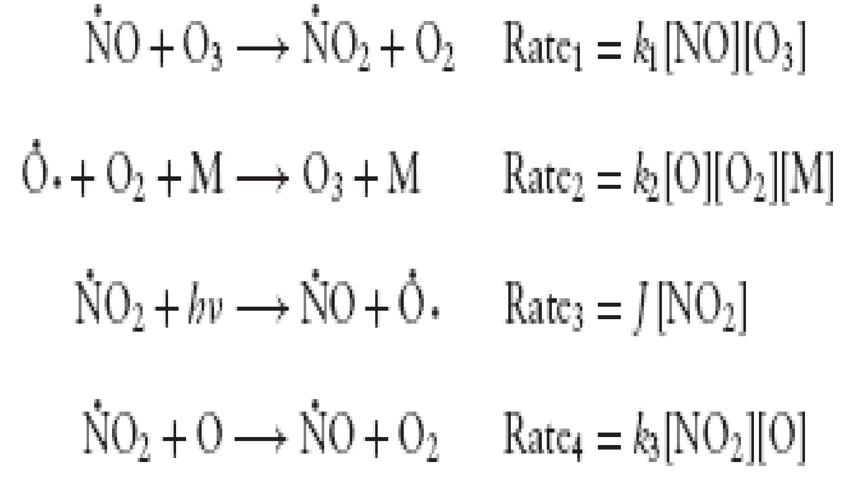
- 1. *Microscale.* Phenomena occurring on scales of the order of 0-100 m, such as the meandering and dispersion of a chimney plume and the complicated flow regime in the wake of a large building.
- *2. Mesoscale.* Phenomena occurring on scales of tens to hundreds of kilometers, such as land-sea breezes, mountain-valley winds, and migratory high- and low-pressure fronts.
- 3. *Synoptic Scale.* Motions of whole weather systems, on scales of hundreds to thousands of kilometers.
- 4. *Global Scale.* Phenomena occurring on scales exceeding $5 \,.\, 10^3$ km.

Spatial Scales of Atmospheric Chemical Phenomena



Phenomenon	Length scale, km
Urban air pollution	1–100
Regional air pollution	10–1000
Acid rain/deposition	100–2000
Toxic air pollutants	0.1–100
Stratospheric ozone depletion	1000–40,000
Greenhouse gas increases	1000–40,000
Aerosol–climate interactions	100–40,000
Tropospheric transport and oxidation processes	1–40,000
Stratospheric–tropospheric exchange	0.1–100
Stratospheric transport and oxidation processes	1–40,000

SETS OF REACTIONS



$$\dot{N}O + O_3 \longrightarrow \dot{N}O_2 + O_2 \qquad \mathrm{Rate}_1 = k_1[NO][O_3]$$

$$\dot{O}\cdot + O_2 + M \longrightarrow O_3 + M \qquad \mathrm{Rate}_2 = k_2[O][O_2][M]$$

$$\dot{N}O_2 + h\nu \longrightarrow \dot{N}O + \dot{O}\cdot \qquad \mathrm{Rate}_3 = J[NO_2]$$

$$\dot{N}O_2 + O \longrightarrow \dot{N}O + O_2 \qquad \mathrm{Rate}_4 = k_3[NO_2][O]$$

- Atmospheric chemical problems require the determination of gas concentrations when many reactions occur at the same time.
- A difficulty arises because a species is usually produced and/or destroyed by several reactions.

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t} &= P_c - L_c = \mathrm{Rate}_3 + \mathrm{Rate}_4 - \mathrm{Rate}_1 \\ &= J[\mathrm{NO}_2] + k_3[\mathrm{NO}_2][\mathrm{O}] - k_1[\mathrm{NO}][\mathrm{O}_3]\end{aligned}$$

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{NO}_2]}{\mathrm{d}t} &= P_c - L_c = \mathrm{Rate}_1 - \mathrm{Rate}_3 - \mathrm{Rate}_4 \\ &= k_1[\mathrm{NO}][\mathrm{O}_3] - J[\mathrm{NO}_2] - k_3[\mathrm{NO}_2][\mathrm{O}]\end{aligned}$$

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{O}]}{\mathrm{d}t} &= P_c - L_c = \mathrm{Rate}_3 - \mathrm{Rate}_2 - \mathrm{Rate}_4 \\ &= J[\mathrm{NO}_2] - k_2[\mathrm{O}][\mathrm{O}_2][\mathrm{M}] - k_3[\mathrm{NO}_2][\mathrm{O}]\end{aligned}$$

$$\frac{\mathrm{d}[\mathrm{O}_3]}{\mathrm{d}t} = P_c - L_c = \mathrm{Rate}_2 - \mathrm{Rate}_1 = k_2[\mathrm{O}][\mathrm{O}_2][\mathrm{M}] - k_1[\mathrm{NO}][\mathrm{O}_3]$$

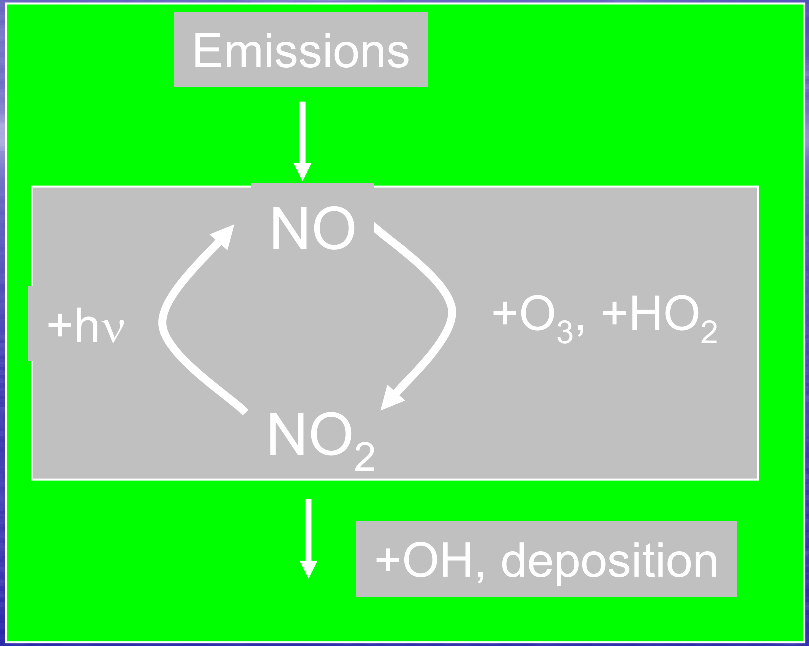
STIFF SYSTEMS

$$\tau_A = \frac{1}{\frac{1}{\tau_{A1}} + \frac{1}{\tau_{A2}} + \cdots \frac{1}{\tau_{An}}}$$

- Gas and aqueous chemical reaction sets are **stiff**.
- Stiff systems of reactions are more difficult to solve numerically than nonstiff systems.
- A **stiff system** of reactions is one in which the **lifetimes** (or time scales) of species taking part in the reactions differ significantly from one another. Species lifetimes are expressed as e-folding or
- half-lifetimes. An **e-folding lifetime** is the time required for a species concentration
- to decrease to 1/e its original value. A **half-lifetime** is the time required for a species
- concentration to decrease to 1/2 its original value.

Chemical Families

Species are grouped together so that the fast reactions don‘t change the group concentration.



Emissions

NO

+hν

$+O_3$, $+HO_2$

NO_2

+OH, deposition

Example:

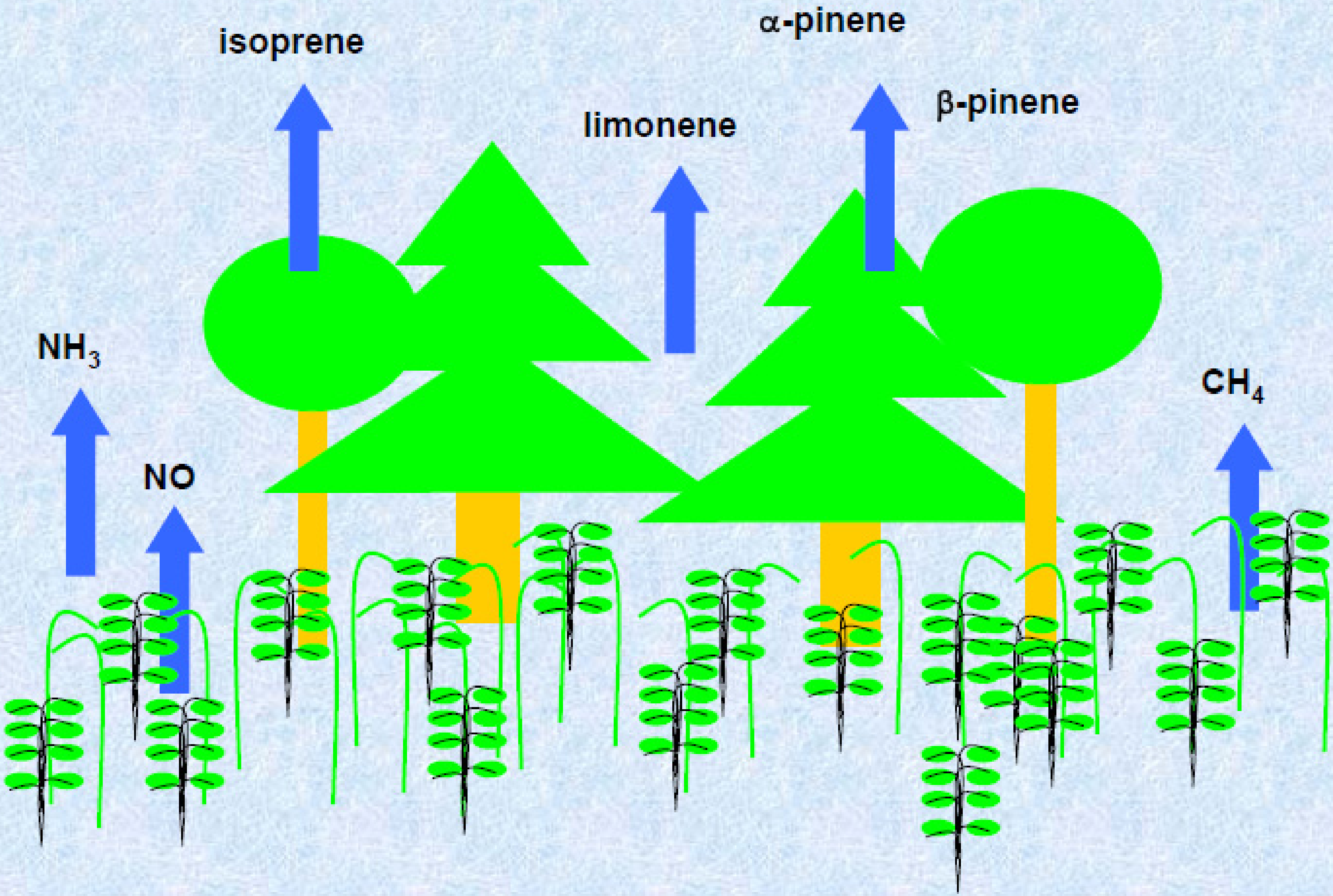
$NO_x = NO + NO_2$

$$\frac{d\mathrm{NO}}{dt} = \mathrm{Emissions} + j_{NO_2} \cdot \mathrm{NO_2} - \mathrm{NO}\left(k_1 \cdot \mathrm{O_3} + k_2 \cdot \mathrm{HO_3}\right)$$

$$\frac{d\mathrm{NO_2}}{dt} = \mathrm{NO} \cdot \left(k_1 \cdot \mathrm{O_3} + k_2 \cdot \mathrm{HO_3}\right) - j_{NO_2} \cdot \mathrm{NO_2} - k_3 \cdot \mathrm{NO_2} \cdot \mathrm{OH} - \mathrm{deposition}$$

$$\frac{d\mathrm{NO_x}}{dt} = \frac{d\mathrm{NO}}{dt} + \frac{d\mathrm{NO_2}}{dt} = \mathrm{Emissions} - k_3 \cdot \mathrm{NO_2} \cdot \mathrm{OH} - \mathrm{deposition}$$

Biogenic Hydrocarbon Emissions



Condensed mechanisms for organic chemistry

- The number of chemical reactions involving organic gases in urban air is large.
- Explicit chemical mechanisms with thousands of organic reactions have been developed (Madronich and Calvert 1989; Jenkin *et al*. 2003; Saunders *et al*. 2003).
- Although such mechanisms can now be solved in a three-dimensional atmospheric model for a period of a few days (e.g., Liang and Jacobson 2000),
- The computational demand for long-term and most practical simulations requires that the number of species and reactions be reduced.

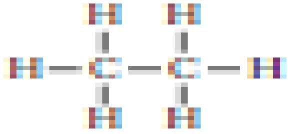
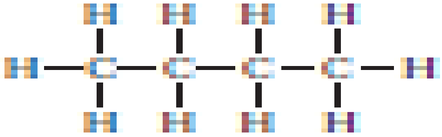
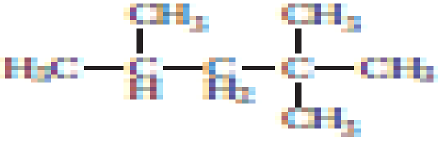
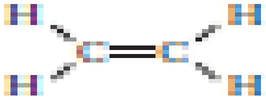
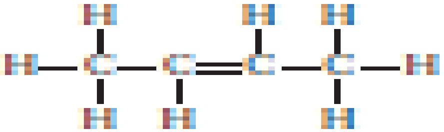
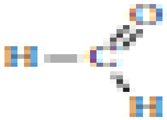
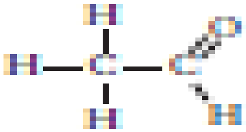
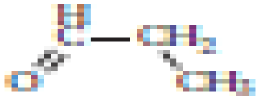
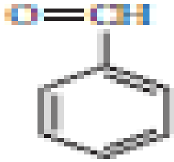
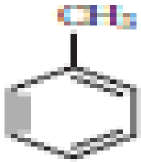
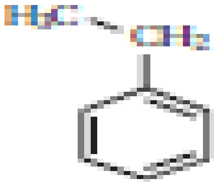
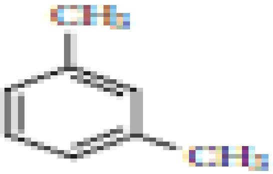
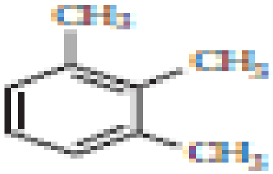
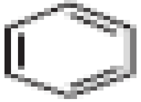
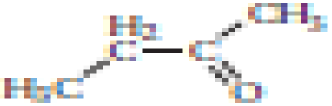
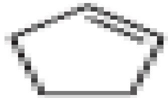
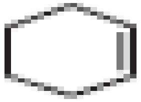
Methods of reducing the number of organic reactions

- Three methods of reducing the number of organic reactions in a model are the carbon-bond lumping method (e.g., Whitten *et al*. 1980; Gery *et al*. 1989),
- The surrogate-species method (e.g., Atkinson *et al*. 1982; Lurmann *et al*. 1987; Griffin *et al*. 2002), and
- The lumped-species method (e.g., Stockwell 1986; Carter 1990, 2000).

Carbon-Bond Lumping Method

- With the **carbon-bond lumping method**, individual organic gases are segregated into one or more bond groups that have similar chemical reactivity.
- For example, a butane molecule, which has four carbons connected by single bonds, is divided into four single carbon atoms, each represented by the **paraffin** (PAR) bond group.

Chemical name
Carbon bond group
Chemical structure

Ethane 0.4 PAR + 1.6 UNR 	*n*-Butane 4 PAR 	2,2,4-Trimethylpentane 8 PAR 	Cyclopentane 5 PAR 
Ethene 1 ETH 	Trans 2-butene 2 ALD2 	Propene 1 PAR + 1 OLE 	Ethyne 1 PAR + 1 UNR $H-C\equiv C-H$
Formaldehyde 1 FORM 	Acetaldehyde 1 ALD2 	Propionaldehyde 1 PAR + 1 ALD2 	Benzaldehyde 1 ALD2 + 5 UNR 
Toluene 1 TOL 	Ethylbenzene 1 PAR + 1 TOL 	*m*-Xylene 1 XYL 	1,2,3-Trimethylbenzene 1 PAR + 1 XYL 
Benzene 1 PAR + 5 UNR 	Methylethylketone 3 PAR + 1 KET 	Cyclopentene 1 PAR + 2 ALD2 	Cyclohexene 2 PAR + 2 ALD2 

- Cyclopentane, which has five single-bonded carbons, is broken into five PAR bond groups. All PAR bonds are assumed to have the same chemical reactivity, regardless of whether they originated from butane or cyclopentane.
- A terminal carbon atom pair with a double bond between the two atoms is represented by an **olefin** (OLE). Nonterminal carbon-atom pairs with a double bond attached to one of the carbons and terminal two-carbon carbonyl groups [C–C(=O)H] are lumped as ALD2.
- Single-carbon ketone groups (C=O) are lumped as KET, seven-carbonaromatics are simulated as **toluene** (TOL), eight-carbon aromatics are simulated as ***m*-xylene** (XYL), and terpenes are grouped as **isoprene** (ISOP).
- **Methane** (CH4), **ethene** (ETH), **formaldehyde** (FORM), **methanol** (MEOH), **ethanol** (ETOH), **acetone** (AONE), and several other species are not lumped.
- Nonreactive carbon atoms in certain organic gases are labeled **unreactive** (UNR).
- In some cases, carbon atoms with a double or triple bond that have similar reactivity to carbon atoms with a single bond are labeled as PAR.

Surrogate-Species Method

- With the **surrogate-species method**, all species of similar reactivity are grouped together.
- Propane and pentane are assumed to have the same reactivity as *n*-butane,
- And all three species are grouped as one surrogate species.

Lumped-Species Method

- With the **lumped-species method**, species of similar reactivity are lumped together, just as with the surrogate species method.
- The difference is that with the surrogate-species method the reaction rate coefficient for each surrogate species is set equal to that of a particular gas.
- The reaction rate coefficient of a lumped species is determined before a model simulation by taking a mole-fraction-weighted average of the reaction rates of each species in the lumped group

Summary of urban chemistry

- Photochemical smog production is governed by emission of oxides of nitrogen and reactive organic gases.
- Emitted gases, called primary pollutants, react in the presence of sunlight to produce secondary pollutants, such as ozone and peroxyacetyl nitrate.
- The radicals that break down emitted reactive organic gases are OH, HO2, O3, NO3 , and O.
- Photolysis also breaks down certain organics.
- Because reactive organic gas radicals compete with O3 to produce NO2 from NO, the photostationary-state relationship does not usually hold in urban air.
- Because gasphase organic chemistry involves reactions among thousands of species, condensed reaction mechanisms have been developed to simplify the simulation of organic chemistry in numerical models.

CHARACTERISTICS OF CHEMICAL EQUATIONS

- Gas-phase chemical reactions are described by first-order, first-degree, homogeneous ordinary differential equations;
- Sets of gas-phase reactions are stiff in that the chemical e-folding lifetimes of individual gases vary by many orders of magnitude.
- Explicit methods result in inefficient (slow) solutions to stiff ODE problems.

Explicit Methods

- With an **explicit method**, final concentrations at time *t* are obtained by evaluating derivatives at the beginning of the current and previous time steps (e.g., at times $t - h$, $t - 2h$, . . .), where a **time step** (s) *h* is the difference
- between the current time (*t*) and the time of the previous time step ($t - h$).
- When an explicit technique is used to solve a stiff set of equations, the time step (*h*) is limited by the e-folding lifetime of the shortest-lived chemical. This lifetime may be 10−6 s or less.
- Time steps longer than the lifetime of the shortest-lived chemical may destabilize the solution scheme.
- When a time step is always small, integration of many reactions over days to months and over a large three-dimensional grid requires a significant amount of computational power and is often impractical.

Implicit Methods

- While in the air, a substance can be chemically altered in one of two ways.
- First, the sunlight itself may contain sufficient energy to break the molecule apart, a so-called photochemical reaction.
- The more frequently occurring chemical alteration, however, takes place when two molecules interact and undergo a chemical reaction to produce new species.
- Atmospheric chemical transformations can occur homogeneously or heterogeneously.
- Homogeneous reactions occur entirely in one phase;
- Heterogeneous reactions involve more than one phase, such as a gas interacting with a liquid or with a solid surface.

Semiimplicit Methods

- Efficient solvers of stiff ODEs are **semiimplicit** in that their solutions at current time *t* depend on derivatives evaluated at the current time, the beginning of the current time step, and/or the beginning of previous time steps (times *t*, *t* − *h*, *t* − 2*h*, . . .).
- Semiimplicit solvers can take time steps much longer than the e-folding lifetime of the shortest-lived species and remain stable.
- Some accurate semiimplicit schemes used for solving stiff ODEs are Gear's method (Gear 1971), Runge–Kutta–Rosenbrock schemes (Kaps and Rentrop 1979; Hairer and Wanner 1991; Press
- *et al*. 1992), and semiimplicit Bulirsch–Stoer schemes (Bader and Deuflhard 1983; Press *et al*. 1992), among others.

Initial value problems

- Problems requiring the use of chemical ordinary differential equations are **initial value problems** whereby the initial concentration of each species is known at time $t = 0$, and a solution is desired at a final time, $t_f > 0$.
- Solutions are found by integrating a set of chemical ODEs one time step (h) at a time between $t = 0$ and $t = t_f$.
- At the beginning of the first time step, concentrations of all species are set to initial concentrations.
- During a time step, an ODE scheme solves for all *gases*.
- Once values at time t are found, t is replaced with $t - h$ and a new time step is solved for.
- With some techniques, solutions depend on concentrations from several time steps backward (times $t - h$, $t - 2h$, . . .).
- If the technique relies on values from two time steps backward, the first time step is solved for with a technique that depends on only one time step backward, and subsequent time steps are solved for with the scheme that depends on two time steps backward

Properties of ODE solvers

- For a chemical ODE solution scheme to be useful, it must be stable, accurate, mass-conserving, positive definite, and computationally fast.
- A numerical scheme is defined to be **stable** if the absolute-value difference between the numerical and the exact solution did not grow over time.
- Solutions must be **accurate** as well as stable. A method of testing a solver's accuracy is to compare the time-dependent solution from it with an exact solution.
- A **normalized gross error** (NGE) is then calculated as

$$\mathrm{NGE} = \frac{1}{N_{\mathrm{tim}}} \sum_{j=1}^{N_{\mathrm{tim}}} \left(\frac{1}{K_{s,t_j}} \sum_{i=1}^{K_{s,t_j}} \frac{\left| N_{i,t_j} - E_{i,t_j} \right|}{E_{i,t_j}} \right) \times 100\%$$

- A solver of chemical ODEs should be **mass-conserving**. A scheme is massconserving if the mass of each element (e.g., N, O, H, or C) summed over all species at the beginning of a simulation equals the mass of the element summed over all species at the end of the simulation, provided no external sources or sinks exist.

Positive definite and fast

- Concentrations predicted by chemical ODE solvers must exceed or equal zero. This should not be a surprise, since in the atmosphere, gas concentrations exceed or equal zero.
- If a scheme always predicts nonnegative concentrations, it is **positive definite**. An accurate chemical ODE solver is usually positive definite, since correct solutions are always nonnegative.
- If a solver is unstable and/or inaccurate, concentrations may fall below zero. If at least one concentration falls below zero after a time step, the time step must either be re-solved with a shorter time step or with a new solution method, or the concentration must be set to zero or above, in which case mass is gained.
- A good solver of chemical ODEs can predict the time step required to keep solutions stable and positive-definite.
- When used in atmospheric models, chemical ODE solvers should be **fast** as well as accurate. All chemical ODE solvers are exactly accurate at a small enough time step.
- A good solver can take a long step and maintain accuracy. For three-dimensional modeling, accuracy with long steps is generally not enough.
- Accurate solutions to chemical ODEs must be found over large model grids.

ANALYTICAL SOLUTIONS TO ODES

$$\dot{N}O_2 + h\nu \rightarrow \dot{N}O + \dot{O}\cdot \qquad (J)$$

$$\frac{d[NO_2]}{dt} = -J\,[NO_2]$$

$$[NO_2]_t = [NO_2]_{t-h}\, e^{-Jh}$$

- The most accurate solution to a set of chemical ODEs is an **analytical solution**.
- Analytical solutions to a single equation or a small set of equations are readily found.
- Whereas the solution to (12.5) was found easily, analytical solutions to a set of
- more than a few equations are usually impractical to obtain. Thus, sets of chemical
- ordinary differential equations are not solved analytically in atmospheric models.

TAYLOR SERIES SOLUTION TO ODES

$$N_{i,t} = N_{i,t-h} + h\frac{\mathrm{d}N_{i,t-h}}{\mathrm{d}t} + \frac{h^2}{2}\frac{\mathrm{d}^2N_{i,t-h}}{\mathrm{d}t^2} + \frac{h^3}{6}\frac{\mathrm{d}^3N_{i,t-h}}{\mathrm{d}t^3} + \cdots$$

- Because analytical solutions are difficult to derive for chemical ODEs, numerical
- solutions are needed. A useful method of solving sets of ODEs would appear to be
- an explicit Taylor series expansion of species concentrations.

Further reading

- **This lecture is based on the materials of the following books that are recommended for further reading**
- J.H.Seinfeld and S.N.Pandis. ATMOSPHERIC CHEMISTRY AND PHYSICS: From Air Pollution to Climate Change. JOHN WILEY & SONS, INC. 2006.
- MARK Z. JACOBSON. Fundamentals of Atmospheric Modeling. Cambridge University Press 2005.
- Daniel J. Jacob. INTRODUCTION TO ATMOSPHERIC CHEMISTRY. Princeton University Press. 1999.

THANKS

FOR

YOUR ATTENTION !!!