

Beltsville PBL Air Quality Modeling Atmospheric Chemistry
Atmospheric Chemistry / Air Quality Box models
(William Stockwell/Rosa Fitzgerald)

Objective: The student will learn about the chemical reactions that occur in the PBL, to write differential equations that describe the resulting chemical change and to solve them using the numeric platform of their choice.

Atmospheric Chemistry in the troposphere.

Figure 1 shows several processes that affect the composition of the troposphere. There is a background composition of oxygen (O₂), nitrogen (N₂), ozone (O₃), water vapor (H₂O), nitrogen oxides (NO_x = nitric oxide (NO) + nitrogen dioxide (NO₂)), methane (CH₄) and other compounds. Much of the background ozone is produced in the stratosphere and transported to the troposphere through processes such as stratospheric folding. In fact, Lin et al, (2015) found that the stratosphere may inject ozone sufficient to degrade air quality to unhealthy levels during the spring at the Earth's surface in the western United States.

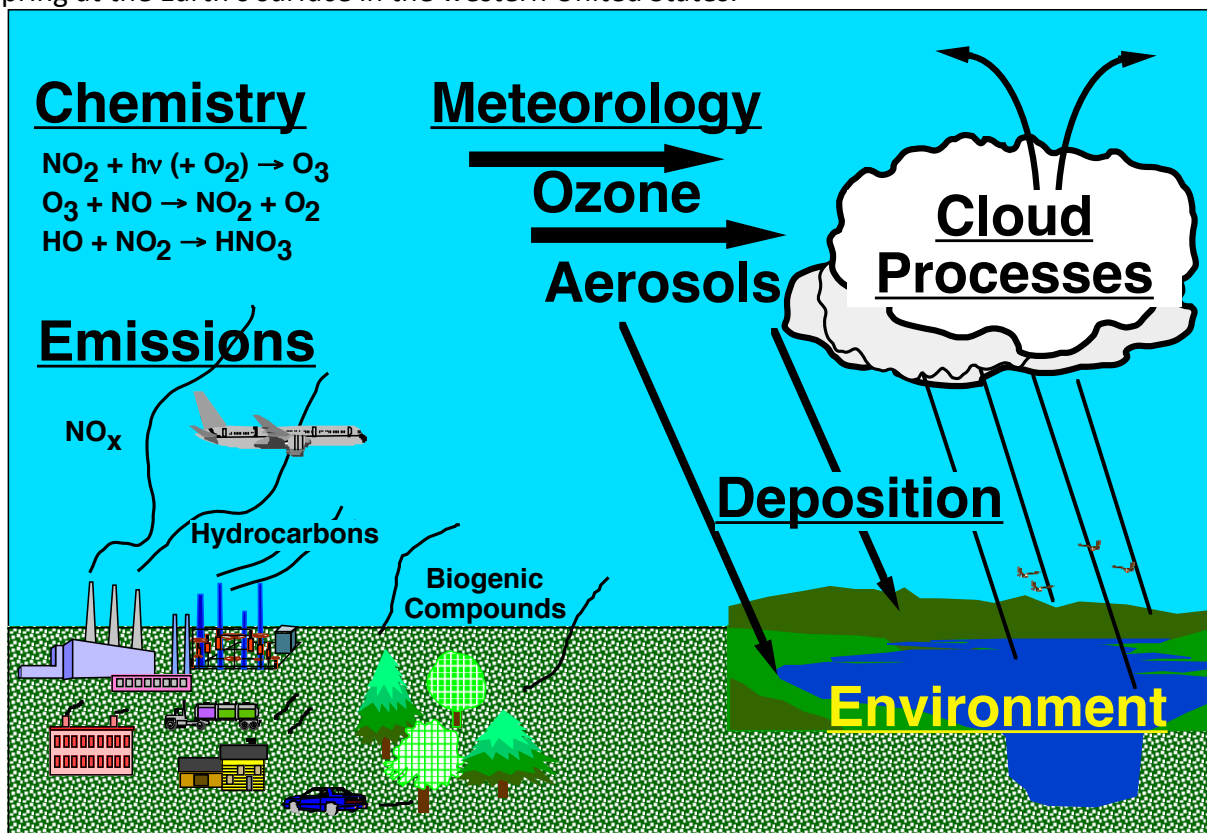
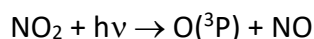


Figure 1. Processes that affect the formation of air pollution in the troposphere. The processes that affect ozone and aerosols (particulate matter) include emissions, atmospheric chemistry, meteorology, clouds and deposition. Clouds affect radiation, aqueous chemistry, precipitation and transport.

Figure 1 shows several processes that affect the composition of the troposphere. There is a background composition of oxygen (O₂), nitrogen (N₂), ozone (O₃), water vapor (H₂O), nitrogen oxides (NO_x = nitric oxide (NO) + nitrogen dioxide (NO₂)), methane (CH₄) and other compounds. Emissions include nitric oxide (NO), volatile organic compounds (VOC) such as anthropogenic hydrocarbons and biogenically emitted organic compounds. Emissions react as will be discussed below to produce ozone and particulate matter. Meteorology affects chemistry through temperature and water vapor concentrations and transport. Dry deposition losses to surfaces occur as air pollutants are transported. When air pollutants encounter clouds the pollutants may be lost through precipitation scavenging. Clouds may transport pollutants vertically too.

Atmospheric Chemical Reactions

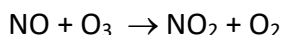
Ozone formation in the troposphere is caused by the photolysis of nitrogen dioxide (NO₂). In the reaction below $h\nu$ represents a photon and O(³P) is a ground state oxygen atom.



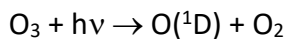
The ground state oxygen atom reacts with molecular oxygen (O₂) to produce ozone. In the equation below M represents another air molecule such as N₂, O₂, Ar, etc. which carries away sufficient energy to allow ozone to form.



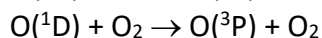
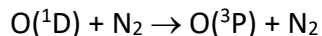
Much of the ozone that forms backreacts with nitric oxide (NO) to reproduce NO₂.



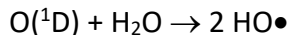
This set of reactions actually recycles O₃ and NO₂. Further conversion of NO to NO₂ produces ozone. This conversion is affected through the hydroxyl radicals (HO•). The HO radical is produced by ozone photolysis which produces an excited oxygen atom, O(¹D).



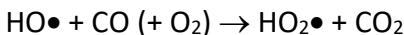
Most of the excited oxygen atoms lose their energy through collisions with N₂, O₂ and other atmospheric gas molecules to reproduce O(³P) that react to reform ozone .



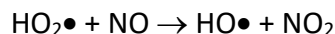
A few of the O(¹D) react with water vapor to produce HO radicals. The dot in the equation below represents an unpaired electron attached to the radical.



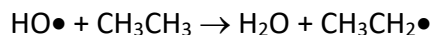
The HO• radical reacts with a number of compounds to produce hydroperoxyl (HO₂•) and organic peroxy radicals (of the form RO₂• where R is any organic group). One reaction that produces HO₂• is the reaction of HO• with CO.



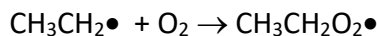
The HO₂• radical reacts with NO to convert it to NO₂ and the NO₂ photolyzes to produce more ozone.



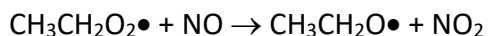
The reactions of HO• with VOC are more important for the conversion of NO to NO₂ and the production of ozone. For example, consider the reaction of HO• with ethane. Ethane is an alkane and the initial reaction for HO• with alkanes is abstraction of a hydrogen to produce water and an alkoxy radical.



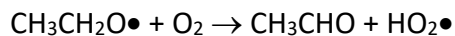
The alkoxy radical reacts with molecular oxygen to produce an organic peroxy radical.



Organic peroxy radicals react with NO to produce NO₂ and an alkoxy radical.

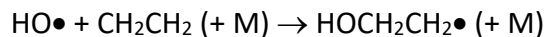


Alkoxy radicals react with molecular oxygen and in the case of the ethoxy radical, acetaldehyde and HO₂• are produced.

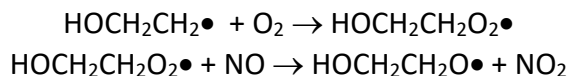


As shown above the HO₂• radicals convert NO to NO₂.

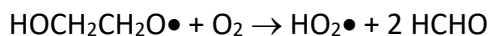
Alkenes, hydrocarbons with double bonds, react similarly with HO• radicals except that the HO• radicals add to the double bond. M, another air molecule, stabilizes the adduct.



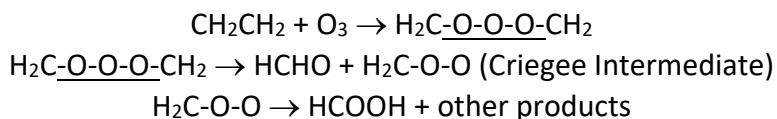
The adduct adds molecular oxygen to produce another peroxy radical that reacts with NO.



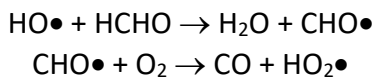
The resulting radical may react with molecular oxygen to produce HO₂• and an aldehyde. In this example formaldehyde is produced.



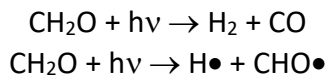
Alkenes also react with O₃ as shown below. The ozone molecule reacts by inserting itself into the double bond. The intermediate breaks up to produce a Criegee intermediate and other products.



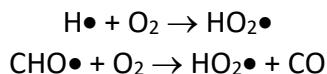
Aldehydes not only reacts with HO• but it also photolyzes. The reaction of HO• follows a scheme similar to those above



Aldehydes have multiple photolysis reactions. In the case of formaldehyde there is a reaction the produces molecular products and another that produces a hydrogen atom and a radical.

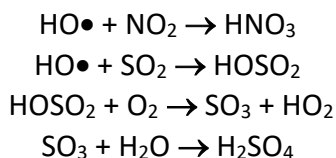


The hydrogen atom and the CHO• radical produce HO₂• radicals and CO.



Other VOC, such as aromatic compounds and biogenically emitted compounds, have chemical reaction schemes with HO• that are much more complicated.

The particulate matter that is produced by atmospheric chemistry may involve both inorganic and organic chemistry. Nitric acid and sulfuric acids are important precursors of inorganic particulate matter. The reactions of HO• with NO₂ and SO₂ produce nitric acid and sulfuric acid, respectively.



Notice that the reaction of HO• with NO₂ removes radicals from the system while the net reaction of HO• with SO₂ propagates them. The produced sulfuric acid initially forms liquid droplets but nitric may remain in the gas-phase.

Further reactions of ammonia (NH₃) with HNO₃ and H₂SO₄ produce solid inorganic particulate matter. In the reactions given below (g) represents the gas-phase, (l) represents the liquid-phase and (s) represents the solid-phase. The arrows pointing in two directions, ⇌, represents equilibrium reactions.

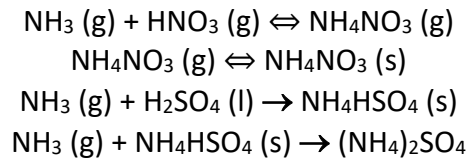


Figure 2 shows an overview of how the reactions discussed in this section fit together. Consider background ozone (top left) as a starting point. Ozone photolyzes to produce the hydroxyl radical (HO•). HO• reacts with CO to produce peroxy-radicals, HO₂• and RO₂•. Peroxy-radicals convert NO to NO₂ and produce other radicals that go on to continue the cycles. The NO₂ produced from NO photolyzes to produce more ozone. Inorganic aerosol is produced from nitric acid, sulfuric acid and ammonia. Secondary organic aerosol is produced from the oxidation of higher molecular weight organic compounds. Radical termination of the HO₂• and RO₂• chains produces hydrogen peroxide (H₂O₂) and organic peroxides (ROOH and ROOR) that may participate in aqueous chemistry in cloud water droplets or on water covered aerosols.

More discussion of atmospheric chemistry for air quality modeling is available in Stockwell et al. (2012).

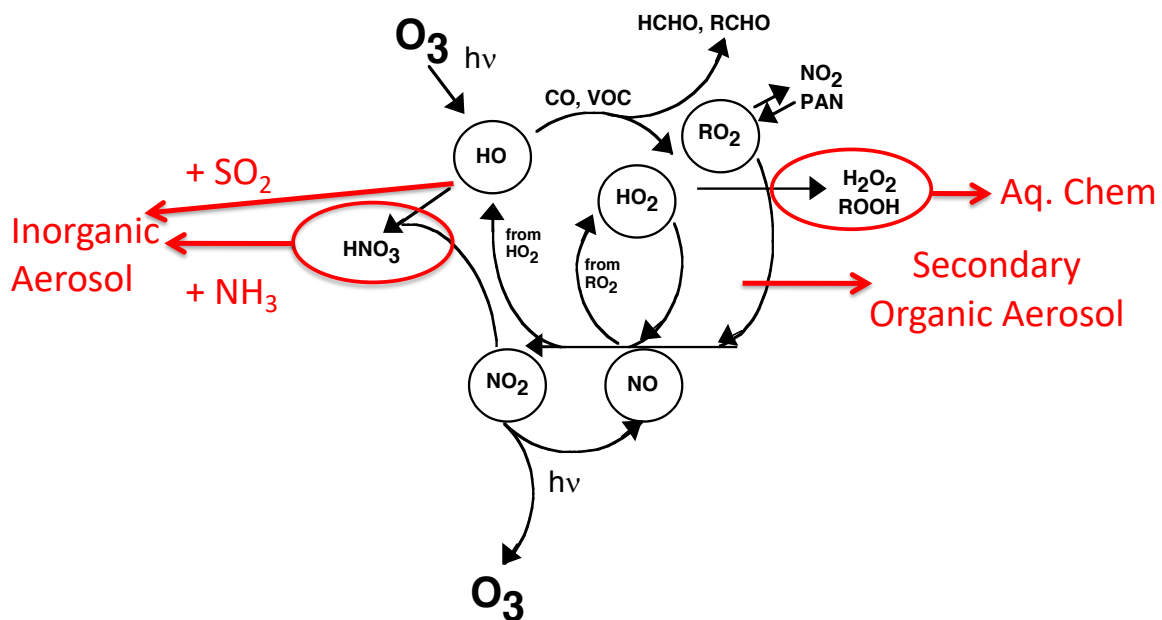


Figure 2. A schematic of the gas-phase atmospheric chemistry that occurs in the troposphere.

Differential Equations for Air Quality Modeling.

Consider this following condensed chemical mechanism from Stockwell and Goliff (2002).

Table 1. Simplified Atmospheric Chemistry Mechanism for the Lower Troposphere

Reaction Number	Reaction	Rate Parameter ^a	k^b	Notes ^c
1	$\text{NO}_2 + h\nu \rightarrow \text{O}(^3\text{P}) + \text{NO}$	Photolysis JNO2	9.35×10^{-3}	1
2	$\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2$	Photolysis JO3	5.33×10^{-5}	1
3	$\text{HCHO} + h\nu \rightarrow 2 \text{HO}_2 + \text{CO}$	Photolysis JHCHOR	3.55×10^{-5}	1
4	$\text{HCHO} + h\nu \rightarrow \text{H}_2 + \text{CO}$	Photolysis JHCHOM	4.91×10^{-5}	1
5	$\text{O}(^3\text{P}) + \text{O}_2 \rightarrow \text{O}_3$	$[\text{M}] \times 5.63 \times 10^{-34} \times (\text{T}/300)^{-2.8}$	1.41×10^{-14}	2, 3
6	$\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O}(^3\text{P}) + \text{N}_2$	$1.8 \times 10^{-11} \times \exp(107/\text{T})$	2.58×10^{-11}	2
7	$\text{O}(^1\text{D}) + \text{O}_2 \rightarrow \text{O}(^3\text{P}) + \text{O}_2$	$3.2 \times 10^{-11} \times \exp(67/\text{T})$	4.01×10^{-11}	2
8	$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{HO}$	2.2×10^{-10}	2.20×10^{-10}	2
9	$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HO}$	$3.1 \times 10^{-12} \times \exp(270/\text{T})$	7.67×10^{-12}	2
10	$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	$1.8 \times 10^{-12} \times \exp(-1370/\text{T})$	1.82×10^{-14}	2
11	$\text{RO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HO}_2 + \text{HCHO}$	4.0×10^{-12}	4.00×10^{-12}	4
12	$\text{CO} + \text{HO} \rightarrow \text{HO}_2 + \text{CO}_2$	$1.3 \times 10^{-13} \times (1 + 2.439 \times 10^{-20} \times [\text{M}] \times (300/\text{T}))$	2.09×10^{-13}	2
13	$\text{HO} + \text{HC} \rightarrow \text{RO}_2 + \text{H}_2\text{O}$	$5.26 \times 10^{-12} \times \exp(-260/\text{T})$	2.20×10^{-12}	5
14	$\text{HO} + \text{HCHO} \rightarrow \text{HO}_2 + \text{CO} + \text{H}_2\text{O}$	$8.6 \times 10^{-12} \times \exp(20/\text{T})$	9.20×10^{-12}	2
15	$\text{HO} + \text{NO}_2 \rightarrow \text{HNO}_3$	$k_0 = 2.50 \times 10^{-30} (\text{T}/300)^{4.4}$; $k_\infty = 1.60 \times 10^{-11} (\text{T}/300)^{1.7}$	8.62×10^{-12}	6
16	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$2.2 \times 10^{-13} \times \exp(600/\text{T}) + 1.85 \times 10^{-33} \times [\text{M}] \times \exp(980/\text{T})$	2.86×10^{-12}	7
17	$\text{HO}_2 + \text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O} + \text{O}_2$	$3.08 \times 10^{-34} \times \exp(2800/\text{T}) + 2.59 \times 10^{-54} \times [\text{M}] \times \exp(3180/\text{T})$	6.42×10^{-30}	7
18	$\text{HO}_2 + \text{RO}_2 \rightarrow \text{ROOH} + \text{O}_2$	$1.66 \times 10^{-13} \times \exp(1300/\text{T})$	1.30×10^{-11}	8
19	$\text{RO}_2 + \text{RO}_2 \rightarrow \text{Prod}$	$1.6 \times 10^{-12} \times \exp(2200/\text{T})$	2.56×10^{-9}	9

^aUnits are as follows: first-order reactions, s^{-1} ; second-order reactions, $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

^bRate parameter at 298 K, 1 atmosphere and local solar noon (latitude = 40°).

^cNotes: 1, *Stockwell et al.* [1997]; 2, *Atkinson et al.* [1999]; 3, rate parameter average of reactions with N_2 and O_2 as third body; 4, rate parameter taken from *Stockwell et al.* [1997, reaction 139]; 5, rate parameter taken from *Stockwell et al.* [1997, reaction 67]; 6, *DeMore et al.* [1997], overall rate constant $k = \{k_0(T)[\text{M}]/(1 + k_0(T)[\text{M}]/k_\infty(T))\} 0.6^{1 + [\log_{10}(k_0(T)[\text{M}]/k_\infty(T))]^2}^{-1}$; 7, *Atkinson et al.* [1997]; 8, rate parameter taken from *Stockwell et al.* [1997, reaction 165]; 9, *Atkinson et al.* [1999], rate parameter of isopropyl radical self-reaction selected.

An example of writing a differential equation the differential equation for HO

The concentration change, $d[\text{X}]/dt$, of any chemically reactive gas-phase species can be written as the difference between the production of X, P_x and its loss, $L[\text{X}]$ terms.

$$\frac{d[\text{X}]}{dt} = P_x - L[\text{X}]$$

For example, we write the differential equation for the hydroxyl radical, HO, for the simple mechanism given in Table 1. The first step is to find the reactions that produce HO and those reactions that remove HO.

Step 1: Reactions that produce or remove HO.

#	Production	#	Loss
8	$O(^1D) + H_2O \rightarrow 2 HO$	12	$HO + CO \rightarrow HO_2 + CO_2$
9	$HO_2 + NO \rightarrow NO_2 + HO$	13	$HO + HC \rightarrow RO_2 + H_2O$
		14	$HO + HCHO \rightarrow HO_2 + CO + H_2O$
		15	$HO + NO_2 \rightarrow HNO_3$

The next step is to write expressions for the rates of each reaction in the table above. Also note the number of HO radicals produced or removed by each reaction. Use square brackets to denote concentrations of the species.

Production and loss rate terms for HO according to the simple mechanism.

#	Production	# of HO produced	#	Loss	# of HO removed
8	$k_8 \times [O(^1D)] \times [H_2O]$	2	12	$k_{12} \times [HO] \times [CO]$	1
9	$k_9 \times [HO_2] \times [NO]$	1	13	$k_{13} \times [HO] \times [HC]$	1
			14	$k_{14} \times [HO] \times [HCHO]$	1
			15	$k_{15} \times [HO] \times [NO_2]$	1

The production and loss rate terms for HO can be used to write the differential equation.

$$\frac{d[HO]}{dt} = HO \text{ Production} - HO \text{ Loss}$$

Note the numbers of HO produced or lost multiply the corresponding terms as shown below.

$$\frac{[HO]}{dt} = 2k_8 \times [O(^1D)] \times [H_2O] + k_9 \times [HO_2] \times [NO] - \{k_{12} \times [CO] + k_{13} \times [HC] + k_{14} \times [HCHO] + k_{15} \times [NO_2]\} \times [HO]$$

Rate Coefficients

First order reactions – Have one reactant such as $NO_2 + h\nu \rightarrow O(^3P) + NO$. The rate coefficient is J_{NO_2} and the reaction has the rate:

$$Rate = J_{NO_2} \times [NO_2]$$

Second order reactions have two reacting molecules that collide and form an energetic intermediate state Figure 3. The intermediate state decomposes to form products.

Bimolecular Reactions

Regular reactions (often produce multiple products).

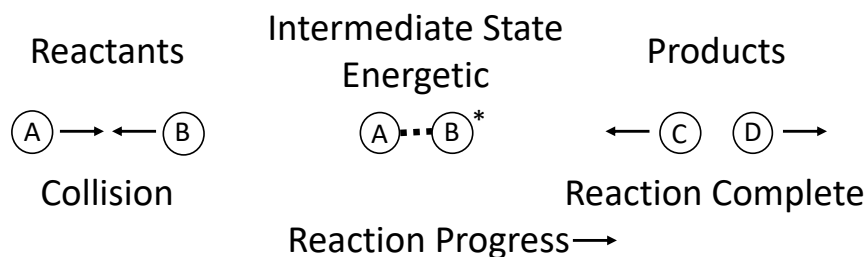


Figure 3. A second order reaction has two reactants. The intermediate state is energetic as marked by the asterisk. The intermediate state decomposes to produce lower energy products.

For a reaction of the form $A + B \rightarrow C + D$, the rate will be given by:

$$\text{Rate} = k_{AB} \times [A] \times [B]$$

The Arrhenius equation is a simple generalized equation for a second order rate coefficient where A is the Arrhenius factor (it can be thought of as a probability factor), E_a is the activation energy, R is the gas constant and T is the temperature.

$$k_{AB} = A \times \exp\left(\frac{-E_a}{RT}\right)$$

The form of this equation may be rationalized as shown in Figure 3.

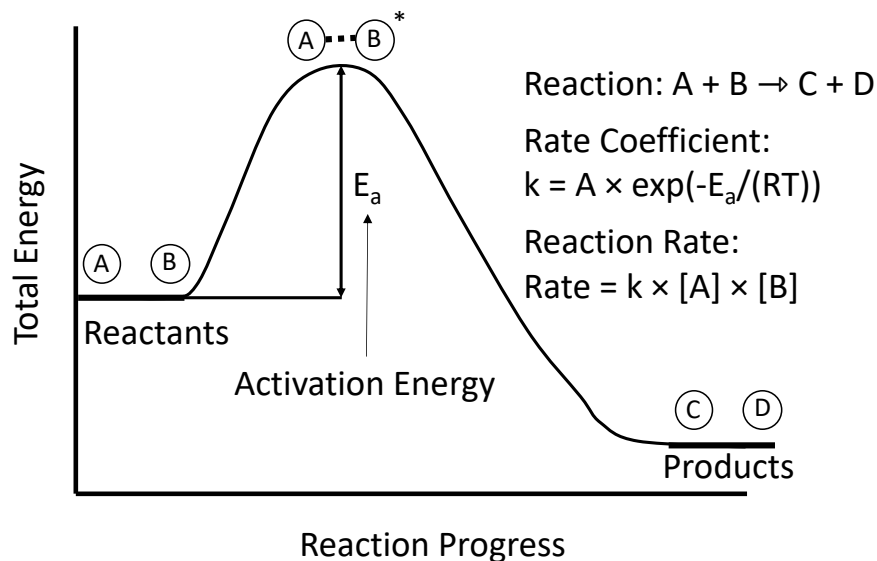


Figure 3. A reaction between two molecules and the relative energy states for the reactants, intermediate and products are shown.

Figure 3 shows that the molecules A and B must collide with a minimum energy, activation energy E_a , to bind together to form an intermediate state. The greater the activation energy the slower the reaction for a given temperature. The intermediate decomposes to form the final products that are of lower energy. This type of reaction that produces products with lower energy than the reactants is known as exothermic (releases energy). Bimolecular reactions that occur in the troposphere are exothermic.

When small molecules collide, they may combine to form a single product as shown by Figure 4.

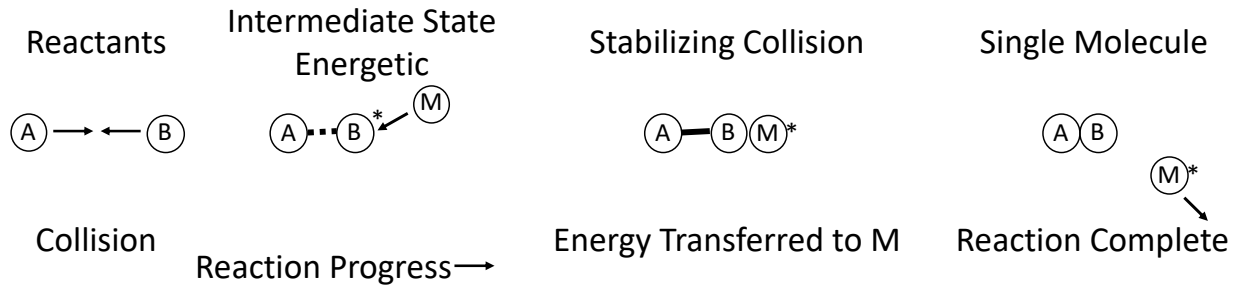


Figure 4. Recombination reactions occur when two small molecules, A and B, react to produce a single product. Following the formation of an energetic intermediate, a second collision between another molecule must occur for the reaction to proceed.

The rate constant for a recombination reaction follows the Troe equation.

$$k = \left\{ \frac{k_o(T)[M]}{(1 + k_o(T)[M]/k_1(T))} \right\} \times F_c^{\{1 + [\log_{10}(k_o(T)[M]/k_1(T))]^2\}^{-1}}$$

Here k_o , k_1 and F_c are constants, $[M]$ is the concentration of molecules in the atmosphere and T is the temperature.

Atmospheric Chemistry Box Models

A chemical mechanism can be translated into a system of ordinary differential equations that characterize chemical changes that occur over time. An atmospheric chemistry box model takes sets of initial conditions and solves the differential equations to yield chemical concentrations. In addition to the initial concentrations files with photolysis frequencies, emissions rates, boundary layer height (box volume) and ventilation rates may be specified depending on the particular model, Figure 4.

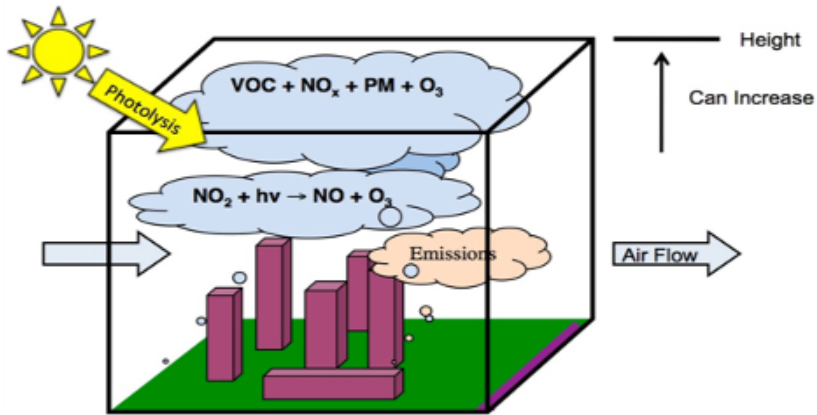


Figure 4. A representation of many of the processes included in a box model.

Note systems of ordinary differential equations for atmospheric chemistry are usually stiff. This means that the numerical methods to solve them may be unstable unless the time step is extremely small. Solutions may become highly inaccurate and they may just numerically blow-up. Special solvers for stiff systems are usually used.

Chemical Isopleths

One use of box models are often used to run a matrix of input conditions, such as a variation in NO_x and VOC, Figure 4. The results can be plotted as 2-d or 3-d contour diagrams called isopleths. Figure 4 shows the effect of initial and VOC on O_3 , H_2O_2 , HNO_3 and hydroxyl HO concentrations. The maxima were cutoff for O_3 , H_2O_2 and HNO_3 so that the structure in these plots may be seen. These plots may be used to estimate the reductions in NO_x and VOC emissions needed to reduce O_3 or particulate matter (HNO_3) concentrations.

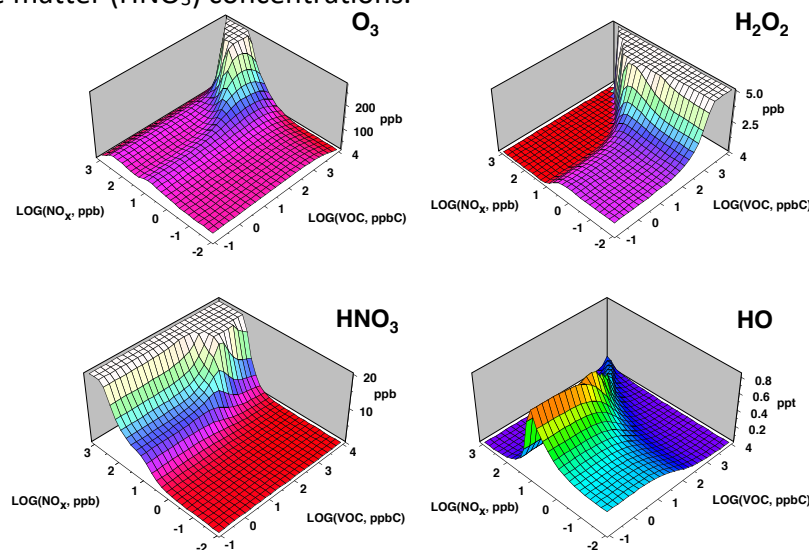


Figure 4. The effect of initial nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and volatile organic compound (VOC) on ozone (O_3), hydrogen peroxide (H_2O_2), nitric acid (HNO_3) and hydroxyl radical (HO) concentrations.

Exercise 3: Building a Box Model for a Condensed Chemistry Mechanism

3A. Write the differential equations for the following chemical species.

$$\begin{array}{ccccc} \frac{[O_3]}{dt} = \dots & \frac{[HC]}{dt} = \dots & \frac{[HNO_3]}{dt} = \dots & \frac{[O(^3P)]}{dt} = \dots & \frac{[HO_2]}{dt} = \dots \\ \frac{[NO]}{dt} = \dots & \frac{[HCHO]}{dt} = \dots & \frac{[ROOH]}{dt} = \dots & \frac{[O(^1D)]}{dt} = \dots & \frac{[RO_2]}{dt} = \dots \\ \frac{[NO_2]}{dt} = \dots & \frac{[H_2O_2]}{dt} = \dots & \frac{[ROOR]}{dt} = \dots & \frac{[HO]}{dt} = \dots & \end{array}$$

Assume that these are constant H_2 , O_2 , N_2 , CO , CO_2 and H_2O ; no differential equation required.

3B. Using the numerical platform of your choice using the initial conditions given in the table below and the J_s (photolysis frequencies you calculated in the first stage of this exercise.

- 1) Try to solve the differential equations numerically using Euler's method or a solver for non-stiff equations.
- 2) Try to solve numerically using a more advanced method for "stiff" differential equations.

Note on Euler's Method

Given a differential equation, in the first case:

$$\begin{aligned} \frac{d[X]}{dt} &= P - L[X] \\ \Delta[X]_i &= (P_i - L_i[X]_i) \times \Delta t \\ [X]_{i+1} &= [X]_i + \Delta[X]_i \end{aligned}$$

Repeat for each differential equation and then advance the time step.

3C. Try to solve the set of equations using a solver for more stiff differential equations and compare with Euler's method.

3D. Determine a range of NO_x and VOC and run sufficient simulations for one day of simulated time to plot isopleths of maximum O_3 , final H_2O_2 , final HNO_3 and maximum HO concentrations.

3F. Plot the isopleths using your numerical platform.

References

Lin, M., A.M. Fiore, L.W. Horowitz, A.O. Langford, S.J. Oltmans, D. Tarasick and H.E. Rieder, Climate Variability Modulates Western US Ozone Air Quality in Spring via Deep Stratospheric Intrusions. *Nat. Commun.* 6, 7105 (2015). doi:10.1038/ncomms8105
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