CHM 5423 – Atmospheric Chemistry
Notes on kinetics (Chapter 4)

Introduction

A mechanism is one or a series of elementary reactions that convert reactants into products or otherwise model the chemistry of a system. Models for the chemical processes taking place in the atmosphere can involve dozens of species and hundreds of elementary reactions. We will often isolate a few of these reactions to focus on particular processes taking place, but in reality there are an enormous number of processes occurring simultaneously in the atmosphere.

There are three types of elementary reactions

unimolecular $\quad$ A $\rightarrow$ "products" $\hfill$ (4.1)

bimolecular $\quad$ A + B $\rightarrow$ "products' $\hfill$ (4.2)

termolecular $\quad$ A + B + C $\rightarrow$ "products" $\hfill$ (4.3)

Notice that the reactions are classified by the number of reactants, and so the particular products do not matter in classifying an elementary reaction.

A sequence of elementary reactions corresponds to a mechanism. For example, the Chapman model for ozone chemistry n the stratosphere is

$\quad$ 1) $\qquad$ $O_2 + h\nu \rightarrow O + O$ $\hfill$ (4.4)

$\quad$ 2) $\qquad$ $O + O_2 + M \rightarrow O_3 + M$ $\hfill$ (4.5)

$\quad$ 3) $\qquad$ $O_3 + h\nu \rightarrow O + O_2$ $\hfill$ (4.6)

$\quad$ 4) $\qquad$ $O + O_3 \rightarrow O_2 + O_2$ $\hfill$ (4.7)

The above mechanism is a chain mechanism. If we define odd oxygen, $O_x = [O] + [O_3]$, then step one produces odd oxygen (and so is an initiation reaction), steps 2 and 3 leave odd oxygen concentration unchaned but convert photons into thermal energy (and so are propagation reactions), and step 4 removes odd oxygen (and so is a termination reaction). Additional reactions can be added to this basic model to give a more refined description of stratospheric ozone chemistry.

For a general reaction with stoichiometry

$\qquad$ aA + bB $\rightarrow$ cC + dD $\hfill$ (4.8)

we can write an expression for the rate of reaction either in terms of the disappearance of a reactant or the appearance of a product

$\qquad$ rate = - (1/a) d[A]/dt = - (1/b) d[B]/dt = + (1/c) d[C]/dt = + (1/d) d[D]/dt $\hfill$ (4.9)

where we choose the sign in such a way as to get a positive value for the reaction rate, and divide by the appropriate stoichiometric coefficient to ensure that we obtain the same rate no matter which reactant or product we monitor.

The observed rate law will often (though not always) fit an equation of the type

$\qquad$ rate = k $[A]^p$ $[B]^q$ $\hfill$ (4.10)

where p is the order of the reaction with respect to A, q is the order of the reaction with respect to B, and so forth. The overall reaction order of the reaction is just the sum of the individual orders, and so in this case would be equal to p + q. Individual reaction orders are usually small nonnegative integers (0, 1, 2) but may on occasion be ratios of

small integers or negative numbers ($^1/_2$, -1). Rates may also depend on product concentrations or th concentration of a catalyst. k in the above expressionis a rate constant, whose value depends only on temperature. Units for k depend on the units used for other quantities in the rate expression. We will typically use units of molecule/cm^3 for concentration, and s for time. There is no direct conection between the reaction orders and the stoichiometric coefficients in the balanced reaction. Note also that not all reactions fit the simple rate law given in eq 4.10.

Termolecular (recombination) reactions.

The most common termolecular reaction is a recombination reaction. The general form of such a reaction is

$$A + B + M \rightarrow AB + M \tag{4.11}$$

Two smaller fragments (atoms or molecules) recombine to form a larger molecule. For example, the recombination reaction that forms ozone is

$$O + O + M \rightarrow O_3 + M \tag{4.12}$$

M, the "third body" collision partner, removes excess energy from the system to stabilize the AB product. The identity of the third body collision partner is relatively unimportant, though different collision partners may differ in their efficiency to stabilize the recombination product.

If the above reaction actually occurred as indicated above than the rate of the reaction would become infinite in the limit $[M] \rightarrow \infty$. However, experimental observations show that at high pressures the rate of reaction becomes constant. That suggests that the actual mechanism for a recombination reaction is more complex than a simple one step process.

The first qualitatively correct model for recombination reactions was proposed by Lindemann, and consists of the following two steps

$$1) \qquad A + B \rightleftharpoons AB^* \tag{4.13}$$

$$2) \qquad AB^* + M \rightarrow AB + M \tag{4.14}$$

A and B combine to form a high energy intermediate AB^*. AB^* can lose energy by collision with a third body M to form a stable product. Otherwise, it will fall apart by the reverse reaction in step 1.

If we assume that the concentration of AB^* reaches an approximately constant value (the stedy state approximation) then

$$d[AB^*]/dt \cong 0 = k_1[A]\,[B] - k_{-1}[AB^*] - k_2[AB^*]\,[M] \tag{4.15}$$

Solving for $[AB^*]$ gives

$$[AB^*] = \frac{k_1[A]\,[B]}{k_{-1} + k_2[M]} \tag{4.16}$$

Since the rate of reaction can be written in terms of the rate of formation of AB, then it follows that

$$\text{rate} = k_2\,[AB^*]\,[M] = \frac{k_1 k_2\,[A]\,[B]\,[M]}{k_{-1} + k_2[M]} \tag{4.17}$$

Notice that eq 4.17 predicts different behavior in the limit of low pressure (when $k_{-1} \gg k_2[M]$) and in the limit of high pressure (when $k_{-1} \ll k_2[M]$). Following the standard method for looking at these reactions, we define an effective bimolecular rate constant, k_{bi}, as

$$k_{bi} = \frac{k_1 k_2[M]}{k_{-1} + k_2[M]} \tag{4.18}$$

The rate of reaction can then be written as

$$rate = k_{bi} [A] [B] \tag{4.19}$$

At high presures the reaction will behave as if it were a true bimolecular reaction (when $k_{bi} \rightarrow k_1$) while at low pressures $k_{bi} \rightarrow (k_1 k_2/k_{-1})[M]$, and the reaction behaves as a true termolecular reaction.

If we invert eq 4.18 we get

$$(1/k_{bi}) = (k_{-1}/k_1 k_2) (1/[M]) + 1/k_1 \tag{4.20}$$

Therefore a plot of $1/k_{bi}$ vs $1/[M]$ will have a slope equal to $k_{-1}/k_1 k_2$ and an intercept equal to $1/k_1$.

Since not all of the individual rate constants in our mechanism can be directly observed experimentally we usually rewrite k_{bi} in terms of k_0 (the low pressure rate constant) and k_∞ (the high pressure rate constant).

$$k_0 = (k_1 k_2/k_{-1}) \qquad k_\infty = k_1 \tag{4.21}$$

If we rewrite k_{bi} in terms of k_0 and k_∞, we get

$$k_{bi} = \frac{k_0 [M]}{1 + (k_0/k_\infty)[M]} \tag{4.22}$$

While the Lindemann model is qualitatively correct, it shows significant differences from what is experimentally observed in recombination reactions, particularly in the region where $k_{-1} \cong k_2[M]$, the "falloff region" where the reaction makes the transition between second order and third order kinetics. Several more sophisticated models for recombination reactions have been developed to better account for the observed behavior of these reactions. The most popular model in atmospheric chemistry, developed by Troe, modifies eq 4.22 as follows

$$k_{bi} = \frac{k_0 [M]}{1 + (k_0/k_\infty)[M]} \quad F_C^{\,x} \tag{4.23}$$

where F_C is a constant, and

$$x = \{ 1 + (\log_{10}(k_0/k_\infty)[M])^2 \}^{-1} \tag{4.24}$$

where the temperature dependence of k_0 and k_∞ is given by the expressions

$$k_0(T) = k_0^{300} (T/300K)^{-n} \tag{4.25}$$

$$k_\infty(T) = k_\infty^{300} (T/300K)^{-m} \tag{4.26}$$

Notice we now have several adjustable constants: F_C, k_0^{300}, k_∞^{300}, n, and m. For atmospheric reactions we usually choose $F_C = 0.6$ (in part for reasons associated with Troe's model) and treat k_0^{300}, k_∞^{300}, n, and m as adjustable parameters whose values are determined by fitting eq 4.23 to experimental data. A similar model can be developed for unimolecular dissociation reactions.

Bimolecular reactions.

The most common reaction in the gas phase is a bimolecular reaction

$$A + B \rightarrow \text{"products"} \qquad rate = - d[A]/dt = k [A] [B] \tag{4.27}$$

For cases where there are some initial concntrations of A and B present in the system the concentratin of A and B change with time according to the relationship

$$1/([A]_0 - [B]_0) \quad \ln\{[A]_t[B]_0/[A]_0[B]_t \} = kt \tag{4.28}$$

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a fairly complicated result. However, such behavior is seldom actually observed in the atmosphere and can usually be avoided in laboratory studies. If the concentration of one of the reactants remains constant, either because a source of the reactant regenerates it as it is removed by reaction or because the initial concentration of one reactant is so much larger than that of the other reactant that its concentration remains approximately constant, then pseudo-first order conditions will apply, and

$$\text{rate} = - d[A]/dt = k'[A] \tag{4.29}$$

where $k' = k\,[B]_0$. In such cases the usual result for first order kinetics occurs

$$[A]_t = [A]_0 \exp(-k't) \tag{4.30}$$

The half life of the reaction, $t_{1/2}$, corresponding to the time it takes for half of the initial concentration of A to disappear, is then

$$t_{1/2} = \ln(2)/k' \tag{4.31}$$

where k' is the pseudo first order rate constant for the reaction. Atmospheric chemists also commonly use a related term, the lifetime (τ), given by the expression

$$\tau = 1/k' \tag{4.32}$$

τ corresponds to the time it takes for the initial concentration to decrease to $1/e = 0.37$ of its original value.

The Arrhenius equation is often used to express the dependence of a bimolecular rate constant on temperature. According to this equation

$$k = A \exp(-E_a/RT) \tag{4.33}$$

where E_a is the activation energy of the reaction, and A, the pre-exponential factor, depends on the collision frequency and the fraction of collisions with an orientation favorable for reaction. A simple analysis using collision theory shows that the Arrhenius equation is approximately correct for cases where the range of temperatures for which it is used is small. Eq 4.33 can be transformed into a linear relationship by taking the logarithm of both sides, giving

$$\ln k = \ln A - (E_a/R)\,(1/T) \tag{4.34}$$

A plot of $\ln k$ vs $1/T$ can therefore be used to find values for A and E_a from experimental data.

In some cases systematic deviations from Arrhenius behavior are observed (as curvature in the plot of $\ln k$ vs $1/T$). In such cases a modified form of the Arrhenius equation is often used

$$k = B\,T^n \exp(-C/RT) \tag{4.35}$$

Collisoin theory suggests that one would expect $n = \frac{1}{2}$ in eq 4.35. However, n, B, and C are usually treated as adjustable parameters whose values are chosen to give the best agreement between the equation and experimental data. Note that an activation energy can still be defined for eq 4.35, as

$$E_a = - R\, d\ln(k)/d(1/T) \tag{4.36}$$

In this case, the activation energy will weakly depend on temperature.

Note also that there are some gas phase reactions where the apparent activation energy for the reaction is negative. This is inconsistent with the simple collision theory model (which requires $E_a \geq 0$), and is usually evidence that the actual mechanism for the reaction is more complicated than a simple bimolecular process.

<u>Laboratory techniques</u>

There are several common techniques for studying important atmospheric reactions in the laboratory. In this section a few of these methods are discussed.

<u>Fast flow kinetics</u>

In a fast flow reactor the two substances involved in a chemical reaction are rapidly mixed together, and the reaction mixture is then pumped through a cylindrical tube under conditions where plug flow occurs. One common design for a fast flow reactor is shown below.


reactant gases

moveable detector
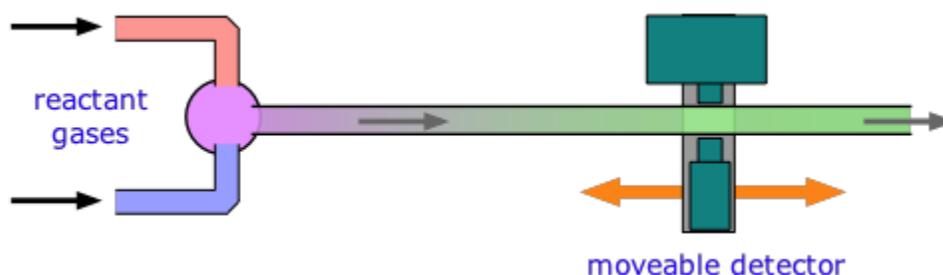
Reactants enter a mixing chamber, where they are rapidly mixed together. The reaction mixture is then pumped through a tube, moving at a constant velocity v. The relationship between d (the distance from the mixing region and the location of the detector) and t (the time after mixing that the reaction has taken place) is

$t = d/v$

Because the gas in the observation zone of the detector is constantly being pumped away and replaced by new gas, the reaction time and the concentration of products and reactants in the observation zone is constant. This means that a slow observation technique (such as absorption spectroscopy or fluorescence) can be used to monitor concentrations of reactants or products. In the above apparatus the detector can be moved along the tube, making it possible to measure concentration as a function of distance from the reaction zone, and therefore as a function of time.

Radical reactions are often studied in fast flow kinetic systems. Several methods can be used to generate radicals. The most common method involves passing a mixture of inert gas and radical precursor through a microwave discharge. The discharge generates reactive species by dissociation. For example, hydrogen and oxygen atoms can be generated in a discharge

$H_2 \rightarrow 2\ H(^2S)$

$O_2 \rightarrow 2\ O(^3P)$
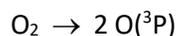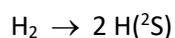
Other reactants can be produced by reaction of the atoms formed in the microwave discharge. As an example, hydroperoxyl radical (HO_2) can be formed by the following sequence of reactions

$H_2 \rightarrow 2\ H(^2S)$

$H(^2S) + O_2 + M \rightarrow HO_2 + M$
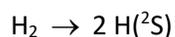
By introducing a mixture of molecular oxygen and an inert gas after the region where the microwave discharge is carried out, hydrogen atoms formed in the discharge can be converted into hydroperoxyl radicals, whose reaction can then be studied. Other radical reactants, including OH radical, can be produced by similar methods.

The major advantage of fast flow techniques is that they do not require fast detection methods. As long as the velocity of gas down the tube and the concentration of reactants entering the mixing zone are kept constant, the concentration of reactants and product in a particular region at a distance d from the mixing region will also remain constant. Absorption spectroscopy can be used to measure reactant or product concentration, but because the narrow diameter of the tube used in fast flow kinetics means a short path length, it is also common to use more sensitive detection techniques, such a fluorescence spectroscopy.

The main disadvantage of fast flow methods are limitations in resolution time and total pressure. A typical flow velocity in a fast flow reaction is v = 1000. cm/s, which means that the distance from the reaction zone (in cm) corresponds to the reaction time (in msec). The method is therefore best suited for studying reactions with half-lives in the region 10-100 msec. To maintain plug flow conditions in the tube, total pressure must be kept between 0.1 – 10 torr. So only reactions that are consistent with these limitations can be investigated in fast flow systems.
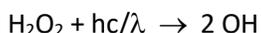
Flash photolysis

An alternative to fast flow is flash photolysis. In a flash photolysis experiment, a short duration high intensity flash of light is used to generate one of the reactive species in a chemical reaction. The disappearance of that species or other reactant or the appearance of product are monitored in real time. Because of advances in fast electronics, coupled with the use of lasers as a short duration photolysis light source, flash photolysis is now the most common method for studying reactions of interest to atmospheric chemists.

A typical flash photolysis apparatus is shown on the next page. A pulse of light from either a conventional flash lamp (such as a high pressure xenon lamp, a good source of continuous light in the near UV region) or a laser is used to photodissociate the precursor molecules that form the reactive species. If the progress of the reaction is monitored by absorption spectroscopy, then light from an analysis lamp is passed through the reaction cell and is detected by a spectrophotometer coupled to a light detector. Resonance fluorescence, where a molecule is selectively excited by a laser or light from an intense continuous light source and its light emission monitored, is an even more common method of detection. Since the flash and subsequent detection of reactants or products takes place of a short time scale (typically μsec or shorter) a controller is used to keep track of the timing of the flash and detector.
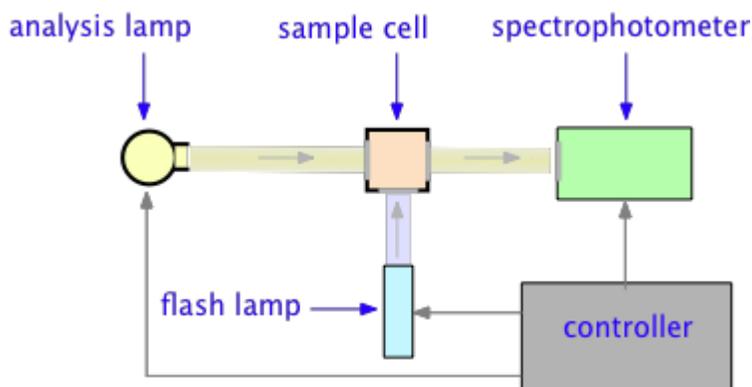
As in the case of fast flow kinetics, a precursor molecule is used as a source of radical reactants. Common precursors are molecules that are themselves relatively inert for the conditions in the reaction cell, and which photodissociate to generate a specific radical with few or no side reactions. For example, hydroxyl radical (OH) can be formed by several methods

$$H_2O_2 + hc/\lambda \rightarrow 2\ OH$$

or

$$O_3 + hc/\lambda \rightarrow O(^1D) + O_2(^1\Delta)$$

$$O(^1D) + H_2O \rightarrow 2\ OH$$
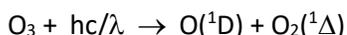
Flash photolysis can be used to study reactions over a much wider range of half lives (μsec and longer) and total pressures (5 – 1000 torr) than fast flow reactors. Because of this, flash photolysis is now the most common method for investigating gas phase reactions of interest to atmospheric chemists.

Relative rate methods

One additional method used to study gas phase reactions is the relative rate method. Consider two molecules (M_1 and M_2) that react with the same species A to form products. If the reaction is bimolecular, then

$$d[M_1]dt = -k_1\ [M_1]\ [A]$$

$$d[M_2]dt = -k_2\ [M_2]\ [A]$$

These equations can be rearranged to give

$$d[M_1]/[M_1] = d\ ln[M_1] = -k_1\ [A]\ dt$$

$$d[M_2]/[M_2] = d\ ln[M_2] = -k_2\ [A]\ dt$$

or

$$(1/k_1)\ d\ ln[M_1]/dt = -[A]$$

$$(1/k_2)\ d\ ln[M_2]/dt = -[A]$$

Since the right hand side of the above equations is the same, the left hand sides must be equal. If we integrate from some initial time zero to a time t, then

$$(1/k_1)\ ln\{[M_1]_t/[M_1]_0\} = (1/k_2)\ ln\{[M_2]_t/[M_2]_0\}$$

or

$$ln\{[M_1]_t/[M_1]_0\} = (k_1/k_2)\ ln\{[M_2]_t/[M_2]_0\}$$

or, finally

$$ln\{[M_1]_0/[M_1]_t\} = (k_1/k_2)\ ln\{[M_2]_0/[M_2]_t\}$$

By plotting $\ln\{[M_1]_0/[M_1]_t\}$ vs $\ln\{[M_2]_0/[M_2]_t\}$ the ratio of rate constants k_1/k_2 can be found. If the value for k_2 is known, then the value for k_1 can be determined.

The main advantage of the relative rates method is that it does not require fast detection methods or even a constant concentration of reactant molecule A. Any method that can be used to monitor the concentration of M_1 and M_2 molecules can be used to follow the progress of the reaction. The method works best when the values for k_1 and k_2 are approximately the same (so that the slope in the data plot is approximately equal to 1).

The main disadvantage of the relative rate method is that it depends on knowledge of the value for k_2. In addition to any uncertainty in the value for the ratio k_1/k_2, uncertainty in the absolute value for k_2 propagates to uncertainty in the value of k_1. Nevertheless, the relative rate method is often used to find rate constants for reactions that are difficult to study by other methods.