Thursday, February 22, 2018

This lecture is a summary of some basics of chemical reaction rate theory, as applied to the atmosphere. This information is not found in many textbooks, including the one for this course (a major weakness, but so it goes). The best summary I have seen is here:

http://acmg.seas.harvard.edu/publications/jacobbook/bookchap9.pdf

If you want to connect to pages in our text, here are a few:

Chapter 3 – page 37-39 (kinetics)
Chapter 5 – page 60-61 (Chapman chemistry)
Chapter 6 – page 67-71 (lifetimes and cycles)
Chapter 9 – page 140-143 (see, especially, Table 9.1)

Bimolecular Reactions

Typically, there are two types of reactions between molecules in the atmosphere that concern us. These are called 2nd order (bimolecular) and 3rd order (termolecular) reactions. We write a generic bimolecular reaction as:

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

The rate at this reaction proceeds can be written as:

$$d[A]/dt = -k^{II} [A] [B]$$

This is called the "law of mass action", where k^{II} is referred to as the "bimolecular rate coefficient" (or more usually, "rate constant"). Note that the sign of the term on the right is negative. This means that [A] is decreasing with time, as it should (it is reacting away).

Because one "A" reacts with one "B" and produces one "C" and one "D", we can also say the following:

$$-d[A]/dt = -d[B]/dt = d[C]/dt = d[D]/dt$$

More General Rate Law

A rate law describes how the disappearance of reactant or appearance of product varies with time.

For a generic reaction that allows for more than one mole of a reactant or product to be consumed or produced:

$$aA + bB \rightarrow cC + dD$$

$$rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Termolecular (three-body) Reactions

Some reactions require three species to react in order to form new products. This is generally the case for reactions that involve the recombination of two species into a new single species, for example, the formation of nitric acid from hydroxyl (OH) and nitrogen dioxide (NO_2):

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

These reactions are called “termolecular”, and they have rate laws that can be written as the following for the general reaction between A, B, and C:

$$\text{Rate} = -d[A]/dt = k^{III} [A] [B] [C]$$

For the reaction above, this becomes:

$$\text{Rate} = d[HNO_3]/dt = k^{III} [OH] [NO_2] [M]$$

Air (or M) is a ‘third body’ for our purposed. It is required to remove excess energy produced in the reaction. This energy, if not removed, would cause the product to fall apart into reactants. N_2 and O_2 are both very efficient at carrying away the energy of the reactants A and B when they collide.

It turns out that nearly all termolecular reactions are really a sequence of bimolecular reactions. We call these steps “elementary” reactions. Unfortunately, most introductory chemistry courses teach that there are various “orders” of reactions. In this case, a bimolecular reaction is second order in concentrations and a termolecular reaction is third order. But this is just an empirical (i.e., working) definition. In fact, when looking at these reactions at the molecular scale we find that they are really a series of individual bimolecular reactions, but that when we stack them all up, they behave like a single reaction of all three reactants at once.

An example of a termolecular reaction that is important in laboratories is:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$rate = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

The rate of the reaction is:

So:

$$\text{rate} = \tfrac{1}{2}\, d[NO]/dt = k\,[NO]^2\,[O_2]$$

What are the units for k^{II} and k^{III}?

On the left hand side, the change in concentration with time (d[A]/dt) is usually expressed in molecules cm^{-3} s^{-1}, so the right hand must be molecules cm^{-3} s^{-1}.

Ignoring the + and – sign

$$k^{II}\ (cm^{3}\ molecule^{-1}\ s^{-1})\ x\ [A]\ (molecule\ cm^{-3})\ x\ [B]\ (molecule\ cm^{-3})$$
$$= d[A]/dt\ (molecules\ cm^{-3}\ s^{-1})$$

$$k^{III}\ (cm^{6}\ molec^{-2}\ s^{-1})\ x\ [A]\ (molec\ cm^{-3})\ x\ [B]\ (molec\ cm^{-3})\ x\ [C]\ (molec\ cm^{-3})$$
$$= d[A]/dt\ (molec\ cm^{-3}\ s^{-1})$$

Thus, k^{II} is in *cm^{3} $molecule^{-1}$ s^{-1}* and k^{III} is in *cm^{6} $molecule^{-2}$ s^{-1}*. It’s a little tricky getting used to units that are inverse concentration, but realize that they don’t represent anything physical, other than the fact that if the bimolecular rate coefficient for one reaction is larger than that for another, it means the reaction with the larger rate constant is more likely to occur when two molecules collide. So the rate constant is just a number that tells us the likelihood that two molecules, when they collide, will react to form products.

Let’s look at an example - the oxidation of methane (CH_4) (Page 65). The reaction between CH_4 and OH starts a whole reaction chain going that ultimately produces some ozone in the troposphere. It will be the one that controls the rate at which cycle will proceed, so we’ll call it the “rate determining step.” What does it actually look like when we put real numbers in for the mixing ratios of CH_4 and OH?

$$-\,d[CH_4]/dt = k^{II}\,[CH_4]\,[OH]$$
$$\sim (1 \times 10^{-14}\ \mathrm{cm^3\ molec^{-1}\ s^{-1}}) \times (2\ \mathrm{ppm}) \times (0.1\ \mathrm{ppt})$$

We need to convert from mixing ratios to concentrations. Let’s assume we are at sea level ($[M] = 2.45 \times 10^{19}$ molec cm^{-3}). So

$$[CH_4] = (2 \times 10^{-6}) \times (2.45 \times 10^{19}\ \mathrm{molec\ cm^{-3}}) \sim 5 \times 10^{13}\ \mathrm{molec\ cm^{-3}}$$
$$[OH] = (0.1 \times 10^{-12}) \times (2.45 \times 10^{19}\ \mathrm{molec\ cm^{-3}}) \sim 2.5 \times 10^{6}\ \mathrm{molec\ cm^{-3}}$$

$$-\,d[CH_4]/dt \sim (1 \times 10^{-14}\ \mathrm{cm^3\ molec^{-1}\ s^{-1}}) \times (5 \times 10^{13}\ \mathrm{molec\ cm^{-3}}) \times (2.5 \times 10^{6}\ \mathrm{molec\ cm^{-3}})$$

$$\boxed{= 1.25 \times 10^{6}\ \mathrm{molec\ cm^{-3}\ s^{-1}}}$$

What is this ‘rate’ is telling us. If this rate were to remain the same with time, it would say that CH_4, at a concentration of 5x 10^{13} molec cm^{-3} would be consumed by reaction of OH in a time, τ, of 4x10^6 s.

That is,

$$\tau = (5 \times 10^{13} \text{ molec cm}^{-3}) / (1.25 \times 10^{6} \text{ molec cm}^{-3} \text{ s}^{-1}) = 4\text{x}10^{6} \text{ s}$$

Consequently, we call τ the “lifetime of methane with respect to reaction with OH.”

Note that 1 day = 86400 s, so this represents a lifetime of 92 days. Because this value is longer than one day, to do this problem more correctly we really should be using the amount of OH averaged over the time and space (i.e., location) of the air parcel that is in question., and an average value for the rate coefficient that takes variations in temperature into account as the air mixes throughout the troposphere. How do we do that?

In practice, rate constants such as k^{II} above are specific to a particular reaction, and they must be measured separately for every reaction. They are then tabulated in a form called the Arrhenius expression.

$$k^{II} = A \, exp\,(-E_a/RT).$$

"A" is called the pre-exponential; it is determined by such things as the size of the molecules that are reacting, the way they come together to form a new bond, and the way old bonds break.

"E_a" is often called the activation energy; it is related to the overall energy of the reaction. The more energy the reactants have (I.e. the warmer the temperature) usually the more likely they are to react. This isn’t necessarily the case, however, as some reactions actually get slower at higher temperatures. However, the majority of reactions are faster at higher temperatures.

Read more about Svante Arrhenius
http://en.wikipedia.org/wiki/Svante_Arrhenius

How large are rate constants for reactions?

Reactions between charged species (“ion-ion” reactions) are incredibly fast if the charges are opposite.

Reactions between charged species and neutral species (“ion-molecule” reactions) are also pretty fast, as the neutral species becomes polarized (i.e. charge within the molecule begins to separate and the molecules looks somewhat charged) as the ion approaches.

Reactions between two radicals (“radical-radical” reactions) can also be very fast because the two unpaired electrons would like to form a new covalent bond. Usually, these reactions occur on every collision. However, these reactions are not as fast as those involving ions, because the ions actually attract each other or other molecules, whereas radicals act more ‘neutral’ – they react IF they hit each other, but they don’t tend to pull other species towards them.

Reactions between radicals and molecules (“radical-molecule” reactions) can be fast, but usually less so than reactions between two radicals. They don’t typically occur on every collision – maybe only in one-in-ten or one-in-100 collisions.

A Note on Lifetimes

Recall that we defined the lifetime of a compound or substance in the atmosphere as the ratio of the amount of the substance (usually in units of concentration) to the rate at which the substance is being reacted away by some other chemical. Let's take a look at what this means for a bimolecular reaction between A and B:

$$A + B \rightarrow C + D \quad \text{rate} = k\,[A]\,[B]$$

The lifetime of A can be written as:

$$\tau = [A]/\text{rate} = [A]/(k\,[A]\,[B])$$

$$\tau = 1/k[B]$$

Molecules rarely react with each other (i.e. “molecule-molecule” reactions are the slowest of them all).

We call the fastest rates for any two reactants "gas kinetic”, meaning that a reaction occurs on every collision. Ion reactions have larger gas-kinetic rate coefficients. We don’t worry about these in the lower atmosphere, since there are so few ionic species present in the gas phase.

For a radical-radical or radical-molecule reaction, a ‘gas-kinetic’ rate coefficient will be no larger than about

$$k \sim 1 \times 10^{-10}\ \text{cm}^3\ \text{molec}^{-1}\ \text{s}^{-1}$$

Most bimolecular reactions have rates between 10^{-11} and 10^{-14} $\text{cm}^3\ \text{molec}^{-1}\ \text{s}^{-1}$

Steady-State Approximation

Very often in atmospheric chemistry we are not interested in a single reaction, but rather in a coupled set of reactions, where the products of one reaction are the reactants in the next. We make the assumption that these gases are in "steady-state"; that is, that their concentrations do not change with time.

For example:

	rate of reaction
$HO_2 + NO \rightarrow OH + NO_2$	$k_1 [HO_2] [NO]$
$OH + O_3 \rightarrow HO_2 + O_2$	$k_2 [OH] [O_3]$

In this pair of reactions, we need to consider what is causing OH and HO_2 to change.

First, let's look at OH. It is produced by the first reaction and consumed by the second one. The rate of the first reaction is

$$\text{Rate1} = k_1[HO_2][NO]$$

and the rate of the second is

$$\text{Rate2} = k_2[OH][O_3].$$

If the concentration of OH is not changing, it must be produced as fast as it is consumed. Thus:

$$d[OH]/dt = 0 = k_1[HO_2][NO] - k_2[OH][O_3]$$

We can make the same argument for HO_2:

$$d[HO_2]/dt = 0 = k_2[OH][O_3] - k_1[HO_2][NO]$$

In the not-too-distant past, accurate measurements of OH and HO_2 were not possible in the atmosphere. People would use relationships like these to assess both their observations and chemical models.

It is easy to rearrange either of the above expressions:

$$0 = k_1[HO_2][NO] - k_2[OH][O_3]$$

$$k_1[HO_2][NO] = k_2[OH][O_3]$$

$$[OH]/[HO_2] = k_1[NO]/ k_2[O_3]$$

Thus, with measurements of ozone and nitric oxide (which are both relatively easy) and temperature (to get the rate constants right), one can estimate the ratio of OH to HO_2.

Sample Problem: The production of ozone in the troposphere requires the photolysis of NO_2, followed by reaction of an oxygen atom with molecular oxygen:

$NO_2 + h\nu \rightarrow NO + O$ $\quad J = 1 \times 10^{-2}\ s^{-1}$

$O + O_2 + M \rightarrow O_3 + M$ $\quad k = 6.1 \times 10^{-34}\ cm^6\ molec^{-2}\ s^{-1}$

If the NO_2 concentration is 2.46×10^{10} molec cm^{-3} and the density, [M], is 2.46×10^{19} molec cm^{-3}, what is the steady-state production rate of ozone?

The only species that we can create a steady-state approximation for here is O, as it is the only one with both production and loss processes.

$$d[O]/dt = J[NO_2] - k[O][O_2][M] = 0$$

The production rate of ozone is: $d[O_3]/dt = k[O][O_2][M]$

But we don't know [O].

However, we can substitute from the steady-state expression for [O]:

$$\begin{aligned} d[O_3]/dt = J[NO_2] &= 1 \times 10^{-2}\ s^{-1} * 2.46 \times 10^{10}\ \text{molec cm}^{-3} \\ &= 2.46 \times 10^{8}\ \text{molec cm}^{-3}\ s^{-1} \end{aligned}$$

How do equilibrium constants relate to rate coefficients?
We'll come back to this when we deal with acid rain

We write an equilibrium expression, with equilibrium constant K_{eq}, as:

$$A + B \leftrightarrow C + D \qquad K_{eq} = [C]\,[D]/\,[A]\,[B]$$

We can break this into a forward reaction and reverse reaction:

$A + B \rightarrow C + D$ rate of forward reaction = $k_f\,[A]\,[B]$

$C + D \rightarrow A + B$ rate of reverse reaction = $k_r\,[C]\,[D]$

At equilibrium, the rates of forward and reverse reactions are equal (or else the concentrations of the species would change). So

$$k_f\,[A]\,[B] = k_r\,[C]\,[D]$$

Rearranging:

$$[C]\,[D]/[A]\,[B] = k_f/k_r = K_{eq}$$

So $K_{eq} = k_f/k_r$, the ratio of two reaction rate coefficients!