

## Photochemistry, Part 2

### Reactions between molecules

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



The rate of this reaction can be written as:

$$d[A]/dt = -k [A] [B]$$

where  $k$  is referred to as the “rate coefficient” or “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). We can also say the following:

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

In practice, rate constants such as  $k$  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.

$$k = A \exp(-E_a/RT).$$

" $A$ " 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.

## Termolecular reactions

Some reactions require three species to react in order for new products to form. 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<sub>2</sub>):



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

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

For the reaction above, this becomes:

$$\text{Rate} = d[\text{HNO}_3]/dt = k [\text{OH}] [\text{NO}_2] [\text{M}]$$

Air, or M, is our usual ‘third body’, as nitrogen and oxygen are very efficient at carrying away the energy of the reactants A and B when they stick together.

## More General Rate Law

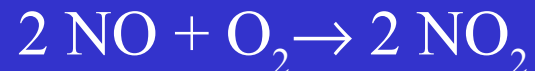
A rate law describes how the disappearance of reactant or appearance of product varies with time.

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



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

Another real example of a termolecular reaction



The rate of the reaction is then:

$$\text{rate} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

So, rate =  $k [\text{NO}]^2 [\text{O}_2]$

## 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 molecule 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:



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

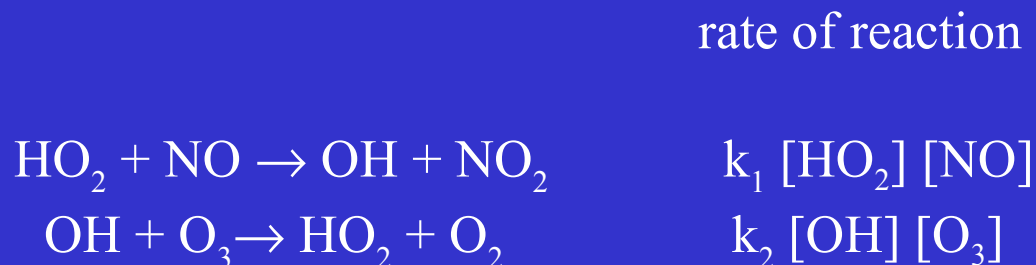
$$k \sim 1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

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:



In this pair of reactions, we need to consider what is causing OH and HO<sub>2</sub> 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

$$\text{Rate1} = k_1[\text{HO}_2][\text{NO}]$$

and the rate of the second is

$$\text{Rate2} = k_2[\text{OH}][\text{O}_3].$$

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

$$d[\text{OH}]/dt = 0 = k_1[\text{HO}_2][\text{NO}] - k_2[\text{OH}][\text{O}_3]$$

We can make the same argument for HO<sub>2</sub>:

$$d[\text{HO}_2]/dt = 0 = k_2[\text{OH}][\text{O}_3] - k_1[\text{HO}_2][\text{NO}]$$

In the not-too-distant past, accurate measurements of OH and HO<sub>2</sub> 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:

$$0 = k_1[\text{HO}_2][\text{NO}] - k_2[\text{OH}][\text{O}_3]$$

$$k_1[\text{HO}_2][\text{NO}] = k_2[\text{OH}][\text{O}_3]$$

$$[\text{OH}]/[\text{HO}_2] = k_1[\text{NO}] / k_2[\text{O}_3]$$

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<sub>2</sub>.

Sample Problem: The production of ozone in the troposphere requires the photolysis of  $\text{NO}_2$ , followed by reaction of an oxygen atom with molecular oxygen:



If the  $\text{NO}_2$  concentration is  $2.46 \times 10^{10} \text{ molec cm}^{-3}$  and the density,  $[\text{M}]$ , is  $2.46 \times 10^{19} \text{ molec cm}^{-3}$ , 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.

$$d[\text{O}]/dt = J[\text{NO}_2] - k[\text{O}][\text{O}_2][\text{M}] = 0$$

The production rate of ozone is:  $d[\text{O}_3]/dt = k[\text{O}][\text{O}_2][\text{M}]$

But, we don't know  $[\text{O}]$ .

However, we can substitute from the steady-state expression for  $[\text{O}]$ :

$$\begin{aligned} d[\text{O}_3]/dt &= J[\text{NO}_2] = 1 \times 10^{-2} \text{ s}^{-1} * 2.46 \times 10^{10} \text{ molec cm}^{-3} \\ &= 2.46 \times 10^8 \text{ molec cm}^{-3} \text{ s}^{-1} \end{aligned}$$

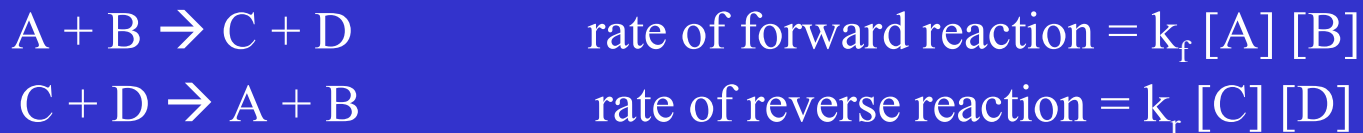
# How equilibrium constants relate to rate coefficients

How does an equilibrium constant relate to reaction rate coefficients?

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



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



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:

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

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