Chemical kinetics in the gas phase

Chemical kinetics is the study of the rates of transformation of chemical compounds from reactant species into products. The rate of a reaction is defined to be the rate of decrease with time of the reactant concentration (in number of moles or molecules per unit volume) due to chemical reaction(s), or, equivalently, the rate of increase of the product concentration. In the atmosphere, chemical reactions typically involve free radicals, as reactants, products or both. Free radicals are neutral fragments of molecules containing an unpaired electron and are generally very reactive. Some important examples include \(\text{OH, HO}_2, \text{HCO, CH}_3,\) and \(\text{CH}_3\text{O}.\) Stable molecules such as \(\text{O}_3, \text{NO}\) and \(\text{NO}_2\) also contain unpaired electrons, which can influence their reactivity.

A. Principles of Chemical Kinetics

A.1 Overall and elementary reactions

The rate is expressed in terms of one mole of reaction, so rates of concentration change are normalized to the reaction stoichiometric coefficients. Thus for the reaction:

\[ a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}, \]

in which \(a, b, c,\) and \(d\) represent the stoichiometric coefficients for their respective compounds in the balanced chemical equation, the rate is defined to be:

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

This expression gives the phenomenological rate at which reactants \(\text{A}\) and \(\text{B}\) are transformed to products \(\text{C}\) and \(\text{D}.\) As such, it contains no information concerning the mechanism of the reaction, nor does it have any predictive utility.

Since most chemical reactions involve an exchange of atom(s) among the reagents, it is intuitive that such processes should proceed via collisions, or at any rate, close approaches of the reagents to one another. Since the likelihood of such collisions increases with number density (concentration), the rate is often expressed in terms of the concentrations of the compounds involved:

\[
Rate = k [\text{A}]^w [\text{B}]^x [\text{C}]^y [\text{D}]^z
\]

where \(k\) represents a concentration-independent factor (which may depend on other parameters; see below). The exact form of this expression must be determined experimentally; any of the species present in the reaction system may appear and the exponents \(w-z\) may or may not bear any relationship to the stoichiometric coefficients \(a-d.\) For example, the low temperature oxidation of methane to carbon dioxide and water, whose balanced equation is:
CH$_4$ + 2O$_2$ $\rightarrow$ CO$_2$ + 2H$_2$O

has a rate expression which may be approximated by:

$$\frac{d[CH_4]}{dt} = -k[M][CH_4][O_2]^{4}[M]^{4}[O_2]^{5}[M]^{5} = -k[M][CH_4][O_2]^{4}[M]^{4}[O_2]^{5}[M]^{5}$$

where [M] represents the total concentration of all species present, and k and k’ are two different constants. This is clearly not intuitively derived from the balanced reaction and indicates that the reaction does not proceed, at a molecular level, by the simultaneous interaction of a methane molecule with two oxygen molecules. A more complex process, involving many individual reaction steps, is responsible for the observed rate expression.

The reaction mechanism is a sequence of elementary chemical reactions, each of which does occur by a single collision between reagents. This sequence of reactions, taken together, must give rise to the observed rate expression. The rate expressions for elementary reactions are easily written from their balanced chemical equations; for example, the elementary reaction:

OH + C$_3$H$_8$ $\rightarrow$ H$_2$O + C$_3$H$_7$,

which is the first step in the atmospheric oxidation of propane, has a rate given by:

$$\frac{d[C_3H_8]}{dt} = -k[C_3H_8][OH]$$

since the reaction takes place by the collision of one OH molecule with one propane molecule. Elementary reactions usually involve free radicals.

A.2. Elementary chemical reactions: general features

If a reaction is known to be elementary, the explicit time dependence of all chemical species involved may be obtained through integration of the rate expression. A few instances are of particular interest in atmospheric chemistry.

(a) First order reactions. These are reactions in which the exponents in the rate expression sum to unity. This class of systems includes photochemical transformations and unimolecular reactions (in the high pressure limit). For example, the rate expression for photodecomposition of formaldehyde in the near ultraviolet,

H$_2$CO + h$\rightarrow$ H + HCO,

is given by:
\[ \frac{d[H_2CO]}{dt} = -k(T, h[H_2CO]) \]

where the rate constant depends on the photon energy as well as temperature. This is easily integrated to yield

\[ [H_2CO]_t = [H_2CO]_0 e^{-kt} \]

a simple exponential decay from the initial concentration, \([H_2CO]_0\).

(b) Second-order reactions. These include bimolecular reactions between different reagents, as well as self-reactions. The rate expression depends upon the instantaneous concentrations of both species involved in the reaction. For example, the reaction of \(OH\) with propane, given above, is second order. The time dependence of reactant concentrations is somewhat more complicated than that for first order reactions:

\[
k_t = \frac{1}{[OH]_0 - [C_3H_8]_0} \ln \left\{ \frac{[OH][C_3H_8]_0}{[C_3H_8][OH]_0} \right\}
\]

In laboratory studies of bimolecular reactions, the concentration of one reagent is typically forced to be in great excess, and so maintains essentially constant concentration during the reaction. For example, if \([C_3H_8] >> [OH]_0\), then \([C_3H_8]_t \approx [C_3H_8]_0\), and rate of change of the \(OH\) concentration becomes

\[ \frac{d[OH]}{dt} = -k(T)[C_3H_8][OH] = k'(T)[OH], \]

where \(k'(T) = k(T)[C_3H_8]_0\). In this case, the reaction is said to exhibit pseudo-first order behaviour, and the time dependence of the \(OH\) concentration is:

\[ [OH]_t = [OH]_0 e^{-k'(T)t} \]

The true bimolecular rate coefficient is then obtained by performing measurements at many different values of \([C_3H_8]_0\), then plotting the observed \(k'(T)\) as a function of \([C_3H_8]_0\). The slope of such a plot yields \(k(T)\).

(c) Third-order reactions. In the atmosphere, many elementary reactions require the participation of three molecules, and are strictly then third order. Important reactions such as:
OH + NO₂ → HONO₂
CH₃ + O₂ → CH₃O₂

require the participation of a “third body” (usually designated as M) to remove the excess energy in the newly-formed product. In the atmosphere, M is generally N₂ or O₂, since these constitute approximately 99% of the atmosphere. The rate expressions of such reactions are properly written as:

\[
\frac{d[HONO₂]}{dt} = k(T)[OH][NO₂][M]
\]

in which the participation of the third body is made explicit. At the higher pressures present in the lower atmosphere, such reactions are often at their high pressure limits: collisions with M are frequent enough that the reaction exhibits pseudo-second order kinetics, with the concentration of M incorporated into the rate constant.

A.3. Sequences of elementary reactions

As mentioned above, the overall reaction mechanism is constructed from a sequence of elementary reactions. These must combine to yield the observed reaction rate expression. Often in such a sequence, a species X is formed as the product of one reaction, and consumed in a subsequent reaction. It can be shown that, if the reaction consuming X occurs much more rapidly than its formation, the concentration of X will be small and almost time-invariant. Here, the rate of formation of X is said to be the rate-limiting step, since X is consumed as soon as it is formed. Under these circumstances, the concentration of X is said to be in steady state. Since the majority of atmospheric radicals are highly reactive, the analysis of their steady state concentrations becomes important.

Consider the sequence of reactions given below, which represent a simplified version of the “oxygen only” chemistry of ozone.

O₂ + h→• → O + O [a]
O + O₂ + M → O₃ + M [b]
O + O₃ → 2O₂ [c]
O₃ + h→• → O₂ + O [d]

The rate of change of the ozone concentration is the difference between the rates of its formation, due to reaction [b], and its consumption, through [c] and [d]. The rate of change of the oxygen atoms is likewise given by the difference between the rates of formation and destruction.
\[
\frac{d[O_3]}{dt} = k_o [O][O_3][M] - k_d[O][O_3] - k_d[O_3]
\]
\[
\]

If the concentrations of these reactive species are time-invariant, the rates of formation and destruction are equal and the steady-state concentrations of each may be calculated:

\[
[O_3]_{ss} = \frac{k_o [O][O_3][M]}{k_o [O] + k_d}
\]
\[
[O]_{ss} = \frac{2 k_o [O_3] + k_o [O_3]}{k_o [O_3][M] + k_o [O_3]}
\]

The measured atmospheric concentrations of O-atoms and ozone are fairly constant over a several hours timescale, under constant illumination from the sun. The analysis given above, although crude, provides a useful picture for how these species’ concentrations depend upon altitude (through the total pressure, related to $[M]$ and the altitude dependence of solar ultraviolet intensities, through $k_a$ and $k_d$).

A.4. Temperature dependence of elementary chemical reactions

The rates of elementary reactions depend upon the reagent concentrations, as discussed above, but also on other parameters, most importantly on temperature. The $T$-dependence of reaction rates is incorporated into $k$, the rate constant (more properly, the rate coefficient). Empirically, it is often found that over the temperature range important in the lower and middle atmosphere $k$ depends on $T$ exponentially:

\[
k = Ae^{-E_{a}/RT}
\]

In this expression, $E_a$ represents the activation energy, $R$ is the gas constant (8.314 J K$^{-1}$ mol$^{-1}$), $T$ is the temperature in Kelvin and $A$ is unimaginatively named the pre-exponential factor. Careful measurements over wide enough temperature ranges reveal that the pre-exponential factor depends weakly on temperature, so is strictly written as $A(T)$. The dependence is generally much weaker than exponential, however, and a temperature-independent value for $A$ is often used. This empirical expression may be interpreted simply as follows: For a chemical reaction to occur, the reagents must collide (i) with sufficient energy to overcome any energy barrier(s) along the reaction path and (ii) in an appropriate geometry to facilitate product formation. The pre-exponential factor contains information concerning the collision rate (dependent upon the reagent velocities, and hence temperature) and any geometric constraints on the reaction. The exponential term arises from consideration of the fraction of collisions, under conditions of thermal equilibrium, which possess energy in excess of some threshold value, $E_{0}$. This energetic threshold is assumed to arise from the presence of energetic “barriers” along the reaction path, due to the energetic.
cost(s) of rearranging the chemical bonds. The activation energy is closely related to threshold energy; for
our purposes they may be taken as equivalent.

An alternate interpretation considers the elementary reaction to occur in two steps: in the first, the
crest of the energetic barrier is achieved; an activated complex (or transition state) is reached. From this
point, the reaction may continue to products, or return to reactants as an unsuccessful collision. If the
activated complexes are held to be in rapid equilibrium with reagent species, with product formation being
rate limiting, a statistical mechanical analysis yields the rate constant in terms of the “partition functions”, Q,
of the reactants (Q_A and Q_B) and the activated complex (designated Q#):

\[ k = \frac{k_B T}{h} \frac{Q^#}{Q_A Q_B} e^{-\frac{E_0/k_B T}{h}} \]

where \( k_B \) is the Boltzmann constant (equal to the gas constant divided by Avogadro’s number) and \( h \) is
Plank’s constant. The partition functions depend only upon molecular properties, such as structure and
vibrational energies, which may be determined spectroscopically or calculated theoretically, allowing
calculation of the rate constant for reaction using the expression above.

This dependence of the rate constant on molecular properties provides an explanation as well for
observed isotope effects in reaction rates. Often it is found that reactions of chemically identical, but
isotopically different species will exhibit different rates, with the heavier isotope displaying the smaller rate
constant. The smaller vibrational frequencies, and thus lower zero-point energy, of the heavier isotope give
rise to somewhat larger reagent partition functions and higher values of \( E_0 \), and hence a smaller rate
constant.

**B. Methods for measuring atmospheric rate parameters**

**B.1 Extracting useful parameters from experiments**

A host of methods is in current use for measuring gas phase reaction rates. The specific technique
employed in any particular case depends somewhat on the particulars of the reaction being studied, and
also on the available apparatus in any given laboratory.

As may be inferred from the forgoing discussion, the object of almost all kinetics experiments is to
determine the reaction rate coefficient, preferably as a function of temperature and also, in the case of
termolecular and unimolecular reactions, of pressure. Very often this is done by following the concentration
of some reactant or product as a function of time, generally under pseudo-first order conditions. The inverse
of the (single exponential) time constants obtained from fits to plots of concentration vs. time are then
plotted as a function of the concentration of the reagent held in excess. This yields the true second order
rate coefficient at a given temperature.

Figure 1 illustrates this situation for a hypothetical reaction between OH and an unspecified hydrocarbon molecule, RH, at 298 K. The reaction of OH with propane, discussed above, is an example of such an OH + RH reaction. Figure 1a shows three plots of the decay of OH as a function of time, following its creation at time = 0. The OH concentration is at all times much smaller than that of RH, ensuring that pseudo-first order conditions are maintained. Curve (i) displays the decay for a low concentration of RH; curves (ii) and (iii) display decays for successively higher RH concentrations. All three exhibit single exponential decays, as required for straightforward pseudo-first order analysis. Figure 1b shows the exponential decay constants obtained from data like that in Figure 1a, plotted as a function of [RH]; the slope of this linear fit gives the bimolecular rate coefficient at 298 K. Note the existence of a finite (positive) intercept, indicating a finite rate of disappearance of OH in the absence of RH. This loss of reagent may be due to wall reactions, reactions of OH with impurities, or self reaction of OH.

Modern experiments yield measurement uncertainties of 5-10% on the rate coefficient at any given temperature. Uncertainties are generally larger at lower temperatures, where the reaction rate is smaller for most reactions. The agreement between different laboratories is usually within 10-20%.

B.2 Experimental techniques

Clearly, the technical issues in measuring reaction rates are: (a) to generate reactive species at some well defined time = 0; (b) to measure accurately the reactant (or product) concentrations as a function of time, over the course of the reaction; (c) to minimize losses of reagent due to processes other than the reaction of interest. Implicit in (b) is the absolute identification of the species whose concentration is being followed. A later section will briefly discuss spectroscopic methods of detection.

(a) Flow tubes. There are two techniques in common use for fairly fast reactions (i.e., those with rate coefficients greater than $10^{-15}$ - $10^{-16}$ cm$^3$ molec$^{-1}$ s$^{-1}$). The flow tube method has several variants, which all share the same basic principles. Reacting gases are entrained in a fast flow of an inert gas (He or N$_2$) at low pressure (a few mbar) passing down a cylindrical tube at constant velocity. One of the reagents is introduced into the flow through a concentric inner tube, (the injector) whose longitudinal position may be varied. The zero-of-time is established when the reagents first come into contact with one another; therefore, varying the position of the injector also varies the exposure of the reagents to one another along the length of the flow tube. Since the reacting mixture moves down the flow tube at constant (known) velocity, exposure length is related to exposure time. The disappearance of reagent(s) and/or growth of product is measured by optical spectroscopy or mass spectrometry as a function of injector position (and hence exposure time) in a volume near the end of the flow tube, before the gas flow enters the pump. Figure 2 illustrates diagramatically a typical flow tube apparatus.

In such methods, reactive atomic or radical species are generated continuously, most often by passing a precursor gas through a plasma generated by a microwave or radio-frequency discharge. This generates atomic reagents directly (i.e., O- or H-atoms from O$_2$ or H$_2$, respectively); these may then react
to form radicals, via processes such as:

\[ H + O_2 + M \rightarrow HO_2 + M; \]
\[ H + O_3 (or NO_2) \rightarrow OH + O_2 (or NO), \]
\[ F + CH_4 \rightarrow HF + CH_3 \]

... etc., that are then introduced into the flow tube. The radical concentrations are generally 1-3 orders of magnitude smaller than those of the molecular reagents, so that a pseudo-first order kinetic analysis is possible.

Recent developments in this technique include the ability to measure simultaneously the concentrations of two radical reagents (and thus to determine radical-radical reaction rates) and the use of higher pressure flow tubes (up to several hundreds of mbar), which allow recombination and other termolecular rates to be measured over a wider pressure regime.

(b) Flash photolysis. Another commonly used method also has several variants; all are based on the early flash photolysis work of Norrish and Porter. Reactive species are generated in a reaction volume by photodissociating a suitable precursor molecule using a short (\# 1 : s) pulse from a laser or flashlamp (almost always a laser nowadays). For example, methyl radicals are generated efficiently by the photolysis of acetone using the 10 ns pulse from a 193 nm wavelength ArF excimer laser:

\[ (CH_3)_2CO + h\rightarrow 2 CH_3 + CO; \]

Similarly, OH may be formed via the 248 nm KrF excimer laser photolysis of nitric acid:

\[ HNO_3 + h\rightarrow OH + NO_2 \]

The precursor species is present in a well-mixed gas mixture which also contains the second reagent and generally a buffer gas as well, which is present to thermalize the photodissociation products prior to reaction. Unless radical-radical reactions are being studied, the photolysis conditions are maintained such that the concentration of radicals remains much smaller than that of molecular reagents. The zero-of-time is established by the pulse of light which creates the reactive species and the decay of the radical concentration (or the growth of product species concentration) is followed as a function of time following that pulse. Measurements are typically made using time-resolved optical spectroscopic methods such as transient absorption or laser-induced fluorescence (LIF) spectroscopy. These methods are discussed below. In the latter variant, (often called the pump and probe method) there is a variable delay time between the firing of the radical-generating laser and the firing of the probe LIF laser, allowing a variable exposure time of the reagents to one another prior to their interrogation. Following each pulse-probe cycle, the reaction volume is replenished with fresh reactants.

Recent developments in this method include the application of time-resolved Fourier-transform
techniques, especially FTIR, with increasingly higher time resolution and sensitivity, and the use of cavity ring-down detection in absorption measurements, with the potential to increase detection sensitivity by many orders of magnitude.

(c) Relative rate determinations. Often, it is more convenient to measure the relative rate of reaction of two reagents with a third reactant, rather than perform an absolute rate determination. For instance, slower reactions, which may suffer from significant artifacts such as wall reactions, may be measured with quite reasonable precision (although not necessarily with great accuracy) in this manner. For a simple set of two competing reactions:

\[
\begin{align*}
A + X & \rightarrow P_1 \\
A + Z & \rightarrow P_2
\end{align*}
\]

it may be easily derived that

\[
\ln \left( \frac{X_0}{X_t} \right) = (k_X / k_Z) \ln \left( \frac{Z_0}{Z_t} \right),
\]

where \(X_0\) and \(Z_0\) represent the respective concentrations at \(t = 0\), \(X_t\) and \(Z_t\) give the concentrations at time “\(t\)” and \(k_X\) and \(k_Z\) represent the two rate coefficients. If one of the rate coefficients is known independently, the other may be determined in this way. Note that reagent “A” need not be measured at all; a similar relationship may be derived for the two product concentrations, meaning that the experimenter may monitor either of the ratios \(X/Z\) or \(P_1/P_2\), depending on convenience, detection sensitivity or other experimental factors.

B.3 Spectroscopic detection methods

Here we present a brief overview of the various methods in common use at the time of writing. All spectroscopic methods rely upon the resonant absorption or emission of radiation in a wavelength region characteristic of the species being detected. The absorption and emission of radiation by atoms and molecules only occurs in particular spectral regions, corresponding to the energy differences between quantum levels. The amount of radiation absorbed by a sample of molecules or atoms at a particular wavelength depends upon an absorption intensity factor \((8)\), which is specific to the atom or molecule and is somewhat dependent upon the temperature, the path length of interaction between the light and the sample, \(l\), and the concentration of absorbing species, \(c\). Under appropriate experimental conditions the inverse of the fraction of incident light transmitted at a particular wavelength, \((I_0/I)\), can be related to the concentration of absorbers, by the Beer-Lambert law:

\[
\ln \left( \frac{I_0}{I} \right) = \sigma (8) l c
\]

As long as the fraction of incident light which is absorbed remains small (ie., less than about 20%), this expression may be manipulated to relate the fraction of light absorbed, \(A(8)\) to the absorber concentration:
This relationship between the amount of light absorbed and concentration, if known, may be exploited to determine the absolute concentrations of reacting species as they change in time during a reaction. Several implementations are in common use. In direct absorption spectroscopy the absorption, \( A(\delta) \), is recorded, either at a specific wavelength, or as a function of wavelength, yielding an absorption spectrum. In flow tube methods, this may take place in a sample cell through which the reacting flow passes downstream of the mixing region; in flash photolysis methods, the absorption is recorded as a function of time after the initial pulse. This variation is commonly known as transient absorption spectroscopy. In its simplest form, a single wavelength, corresponding to a particular absorption feature, is transmitted through the sample, using resonance lamps or lasers. The time-resolved change in the intensity of this source after it has passed through the sample is measured following the initiation of reaction. Depending upon the exact experimental configuration used, the time resolution can be very good (up to \( 10^{-12} \text{ s} \)); more typically it lies in the \( 10^6 - 10^{14} \text{ s} \) range. This technique is readily coupled to long-pathlength absorption cells to yield very sensitive concentration measurements. Modern variations involve the use of tunable diode lasers (TDLs) and cavity ring-down (CRD) systems. Under some fortunate circumstances, a multi-wavelength technique such as FTIR may be used to identify all reactants and products simultaneously as the reaction proceeds. However, the sensitivity is not particularly high, nor is the time resolution, so this method is generally limited to slower reactions, often those being studied in environmental chambers.

A more sensitive, but less general spectroscopic probe of concentrations involves the measurement of some quantity related to the amount of light absorbed. Many atoms and molecules re-emit some fraction of the initially absorbed light, often at a wavelength shifted away (to the red) of the absorbing wavelength. This re-emission forms the basis of resonance fluorescence (RF) spectroscopy and of laser-induced fluorescence (LIF) spectroscopy. The fraction of light absorbed by a sample which is re-emitted depends upon many variables, but remains constant if experimental conditions do not change. The intensity of emitted light is thus a very sensitive proxy for the amount of absorption. Although it is extremely difficult to relate the emission intensity to absolute concentrations, the time-dependence of emission intensity does track that of concentration, so that rates may be determined.

In RF spectroscopy, an atomic resonance lamp optimized for atom X is used to illuminate the sample; emission is observed from any atomic X which is present. Reactions of atomic species such as Cl and ground state O have been studied using such lamps. LIF spectroscopy generally utilizes a tunable laser source to scan over the absorption spectrum of a molecule of interest. When the laser wavelength is resonant with a molecular absorption transition, emission from the excited molecules may be observed. The OH radical is especially well suited to LIF detection and this is the method of choice in studying its kinetics.

Another detection method which is based on measuring emission intensity relies upon the formation of electronically excited products from a chemical reaction. The emission of light from such excited products is known as chemiluminescence; its intensity is related to the concentration of electronically
excited products formed in the reaction. For example, the time dependence of the concentration of ground state oxygen atoms may be followed by detecting emission from electronically excited NO₂, formed in the chemiluminescent reaction:

\[
\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2^* + \text{M} \\
\text{NO}_2^* \rightarrow \text{NO}_2 + h<
\]

Other spectroscopic detection methods, which are no longer in such common use, include *laser magnetic resonance* (LMR) and *electron-spin resonance* (ESR) spectroscopy. Both rely upon the ability of an external magnetic field to perturb the energy levels of an atom or molecule. By varying the magnetic field strength, optical transitions may be brought into resonance with a fixed-wavelength light source, allowing light absorption (and hence detection) to occur.
Figure 1: Extraction of a bimolecular rate coefficient from experimental pseudo-first order reaction conditions, using the OH + RH -> H₂O + R reaction as an example. (a) Decay of OH as a function of exposure time to RH. Curves (i), (ii) and (iii) display the result for increasing RH concentration. (b) The pseudo-first order rate coefficient obtained from fits to data such as that shown in (a), plotted as a function
of the (constant) RH concentration. The slope of the linear fit to these data gives the true second order rate coefficient.

**Figure 2:** Schematic of a flow tube apparatus. Reagents and a carrier gas are introduced from the gas reservoirs (GR) into the flow tube. One reagent is introduced through the movable injector tube (Inj), the other gas flow passes through a microwave discharge cavity (MW), where an atomic or radical reagent
is formed from its precursor compound. The concentration of radical reactant (or of product) may be monitored using the tunable diode laser (DL) - detector (D) combination. The total pressure in the flow tube is monitored at point P.