Chemical kinetics

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Introduction

- In chapter 3, we solved the problem of chemical reaction equilibrium, i.e. how chemical reaction will take place at infinitely long time.
- It does not deal with the problem of how fast/slow the chemical reaction takes place, or chemical reaction rates.
- Chemical reaction rates control
  - The rate of combustion
  - Pollutant formation and destruction
  - Ignition and flame extinction
- Chemical kinetics study elementary reactions and their rates

$$Rate = \frac{\text{change in concentration}}{\text{change in time}}$$

The concentration can increase (products) or decrease (reactants)

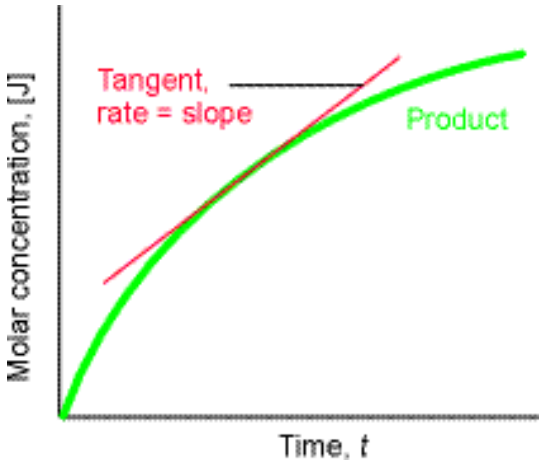
$$A + B \rightarrow C$$

$$Rate = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$$

Or if

$$2A + B \rightarrow 3C$$

$$Rate = -\frac{\Delta[B]}{\Delta t} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = \frac{1}{3}\frac{\Delta[C]}{\Delta t}$$



- Consumption rate of a reactant is -d[R]/dt
- Formation rate of a product is d[P]/dt

Some examples

$$H_2(g) + \frac{1}{2} O_2 \rightarrow H_2O\ (l) \Rightarrow \text{very slow}$$

$$N_2O(g) \rightarrow N_2\ (g) + \frac{1}{2} O_2\ (g) \Rightarrow \text{slow}$$

- Combustion reaction $\Rightarrow$ rapid process
- TNT explosion $\Rightarrow$ very rapid process
- Food spoilage $\Rightarrow$?
- Medicine decompose $\Rightarrow$?

Consider: what parameters will affect the reaction rates.

- Reactants concentration C
- Temperature T
- Catalyst existence and concentration
- Solid, liquid or catalyst contact surface area A

Global versus elementary reactions

Consider an overall reaction of a mole of fuel with a mole of an oxidiser to form b mole of combustion products. This reaction can be expressed by the **global reaction mechanism**:

$$F + aO_x \rightarrow bPr$$

By experiments, the rate at which the fuel is consumed can be expressed as

$$\frac{d[X_F]}{dt} = -k_G(T)[X_F]^n[X_{O_x}]^m$$

Here $[X_i]$ is used to denoted the molar concentration (kmol/m^3) of the ith species in the mixture.

- The constant of proportionality k_G is called the **global rate coefficient**. It's in general NOT a constant, but a strong function of temperature.
- The minis sign indicate the concentration decreases with time (reactants).
- The power n and m relate to the **reaction order**. For global reactions, they are not necessarily integrals but curve-fitting from experiments. We say this reaction is nth order with respect to the fuel and mth order with respect to the oxidiser.
- Different expression of $k_G(T)$ and different value of n and m may apply to cover a wide range of temperature.

Elementary reactions

The use of global reaction in a specific problem is frequently a “black box” approach.

It does not provide a basic understanding of what is actually happening.

In reality, many sequential processes can occur involving many intermediate species. For example consider the following global reaction

$$2H_2 + O_2 \rightarrow 2H_2O$$

This reaction involves the following *important* **elementary reaction**:

$$H_2 + O_2 \rightarrow HO_2 + H$$

$$H + O_2 \rightarrow OH + O$$

$$OH + H_2 \rightarrow H_2O + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

When oxygen and hydrogen molecules collide and react, they do not yield water directly. They form the intermediate species HO_2 (hydroperoxy) radical, and a hydrogen atom, H, another radical.

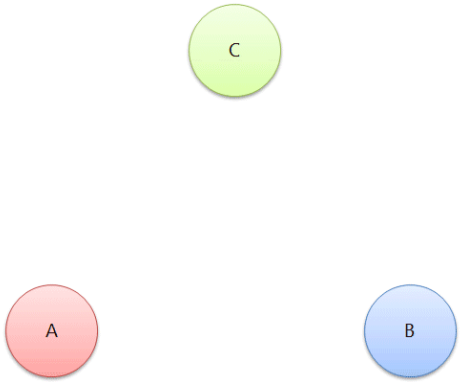
Radicals or **free radicals** are reactive molecules, or atoms, that have unpaired electrons.

Elementary reactions

- In this reaction $H_2 + O_2 \rightarrow HO_2 + H$, to form HO_2 from H_2 and O_2, only one bond is broken and one bond formed.
- We might also consider to form to hydroxyl radicals $H_2 + O_2 \rightarrow 2HO$
- This reaction however is unlikely because it needs to break two bonds and create two new bonds.
- To have a complete picture of $2H_2 + O_2 \rightarrow 2H_2O$ combustion, we need more than 20 elementary reactions.
- The collection of elementary reactions necessary to describe an overall reaction is called a **reaction mechanism**.
- A reaction mechanism may involve from several to several hundred steps. To find minimum steps to describe a particular reaction is an active research area.

Elementary reactions

Unimolecular reactions



Termolecular reactions

Bimolecular reactions

Bimolecular reactions and collision theory

Most elementary reactions of interest in combustion are **bimolecular**.

Two molecules collide and react to form two different molecules

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

The rate at which the reaction proceeds is directly proportional to the concentration (kmol/m^3) of the two reactant species

$$\frac{d[A]}{dt} = -k_{bimolec}[A][B]$$

?

All elementary bimolecular reactions are overall second order, being first order with respect to each of the reactant species. The rate coefficient, $k_{bimolec}$ $(m^3.kmol^{-1}.s^{-1})$, is a function of temperature, and have theoretical basis (unlike global rate coefficient).

Molecular collision theory provides an insight into the equation and suggest temperature dependence of the rate coefficient, but also has many shortcomings.

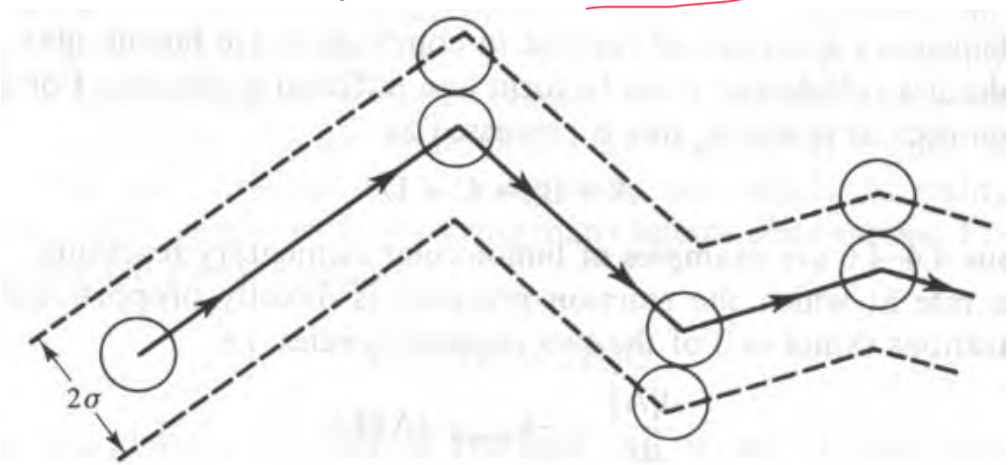
We have introduced the concepts of wall collision frequency, mean molecular speed and mean free path (in mass transfer).

We assume:

- A single molecule of diameter of σ traveling with constant speed v. It collides with identical but stationary molecules.
- If the mean free path (distance between collisions) is large, the moving molecule sweeps out a cylindrical volume in which collisions are possible in time interval of Δt. The volume is $v\pi\sigma^2\Delta t$.
- The stationary molecules are distributed randomly and have a number density of n/V

The number of collisions by the moving molecule per unit time:

$$Z \equiv \frac{collision\ per}{unit\ time} = \left(\frac{n}{V}\right) v\pi\sigma^2$$



In an actual gas, all the molecules are moving. Assuming Maxwellian velocity distribution, the collision frequency for identical molecules is given by

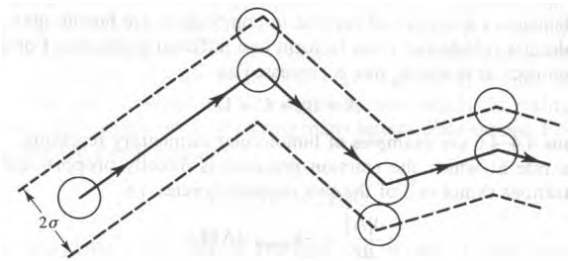
$$Z_c = \sqrt{2}(n/V)\pi\sigma^2\bar{v}$$

Where $\bar{v}$ is the mean speed depends on temperature.

The above equation applies to identical molecules. We can extend this analysis to collisions between two different molecules with diameters of σ_A and σ_B. The diameter of collision volume is then $\sigma_A + \sigma_B \equiv 2\sigma_{AB}$.

The above equation becomes:

$$Z_c = \sqrt{2}(n_B/V)\pi\sigma_{AB}^2\bar{v}_A$$



This expresses the frequency of collision of a single A molecule with all B molecules.

But we are interested in the collision frequency associated with all A and B molecules. This can be obtained by multiplying the collision frequency of a single A molecule (above) with the number of A molecules per unit volume and using appropriate speeds, which is:

$$Z_{AB}/V = \frac{\text{No. of collisions between all A and B}}{\text{Unit volume} \cdot \text{unit time}}$$

$$= (n_A/V)(n_B/V)\pi\sigma_{AB}^2(\bar{v}_A^2 + \bar{v}_B^2)^{1/2}$$

And with a variable of temperature:

$$\bar{v} = \sqrt{\frac{8k_BT}{\pi m}}$$

$$Z_{AB}/V = (n_A/V)(n_B/V)\pi\sigma_{AB}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}$$

Where k_B is Boltzmann constant, $1.381 \times 10^{23}\ J/K$

$$\mu = \frac{m_A m_B}{m_A + m_B} = \frac{\text{reduced mass where } m_A \text{ and } m_B \text{ are the masses}}{\text{of species A and B, respectively, in kilograms;}}$$

T is the absolute temperature (K)

Note: the average speed is obtained by replacing the mass of the single molecule in the following equation with reduced mass μ

$$\bar{v} \equiv \frac{\text{mean speed of}}{\text{species A molecules}} = \left(\frac{8k_BT}{\pi m_A}\right)^{1/2}$$

Wall collision frequency $\quad \frac{1}{4} n$

To relate the above equation to reaction rate, we have

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = [\frac{\text{No. of collisions A and B molecules}}{\text{Unit volume} \cdot \text{unit time}}] \cdot [\frac{\text{probability that a collision leads to reaction}}{}] \cdot [\frac{\text{kmol of A}}{\text{No. of molecules of A}}]$$

Or

Collision Probability

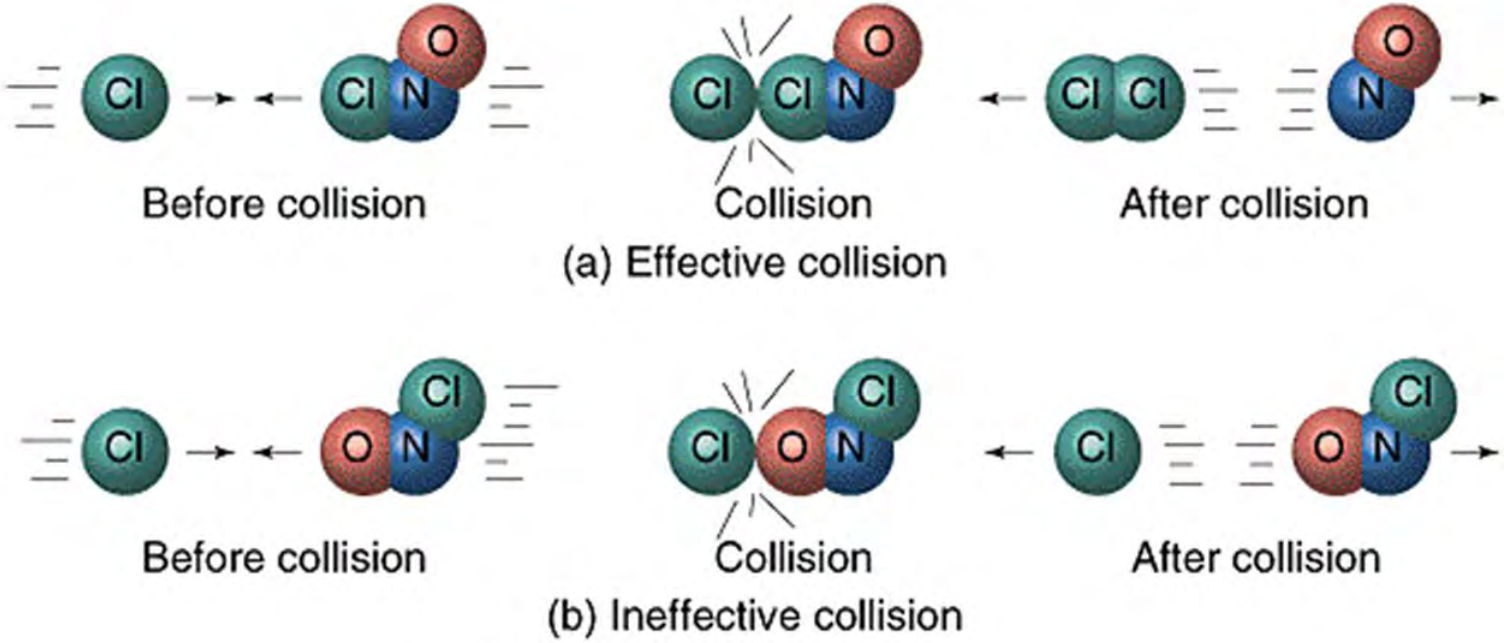
$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = \boxed{(Z_{AB}/V)}\boxed{P}N_{AV}^{-1},$$

Where N_{AV} is Avogadro number ($6.022 \times 10^{23}\ molecules/kmol$)

The probability that a collision leads to reaction depends on two factors (can be expressed as the product of): P

- An energy factor, $\exp[-\frac{E_A}{R_0 T}]$, which expresses the faction of collisions that occur with an energy above the threshold level necessary for reaction E_A, or **activation energy**.
- A geometric or **steric factor**, **p**, that takes into account of the geometry of collisions between A and B: much less than unity, but with exceptions.

A visualisation of steric factor



With the two factors, the previous equation becomes

$$-\frac{d[A]}{dt} = \boxed{pN_{AV}\sigma_{AB}^2\left[\frac{8\pi k_B T}{\mu}\right]^{\frac{1}{2}}\exp\left[-\frac{E_A}{R_0 T}\right]}[A][B]$$

With $n_A/V = [A]N_{AV}$ and $n_B/V = [B]N_{AV}$ being employed.

So we have the bimolecular rate coefficient

$$\boxed{\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k_{\mathrm{bimolec}}[\mathrm{A}][\mathrm{B}]}$$

$$k(T) = pN_{AV}\sigma_{AB}^2\left[\frac{8\pi k_B T}{\mu}\right]^{\frac{1}{2}}\exp\left[-\frac{E_A}{R_0 T}\right]$$

Problem is that the collision theory provides no means to determine the activation energy and the steric factor.

There are more advanced theory, i.e. the activated complex, do allow calculation of $k_{bimolec}$ from the first principle (see below). Not in the scale of this course.

* Gardiner, W.C. Jr, Rates and Mechanisms of Chemical Reactions, Benjamin, MenloPark, CA, 1972

* Benson, S.W., The Foundations of Chemical Kinetics, McGraw-Hill, New York, 1960

If the temperature range of interest is not too great, the bimolecular rate coefficient can be expressed by the empirical **Arrhenius Form**:

$$k(T) = A \exp\left(-\frac{E_A}{R_0 T}\right)$$

Where A is a constant termed the **pre-exponential** of the **frequency factor**.

In fact, A is not strictly constant but depends on $T^{1/2}$.

Arrhenius plot (log k vs. 1/T) by experimental data is used to extract values for the activation energy, because the slope of such plots is $-\frac{E_A}{R_0}$.

Although experimental values are tabulated, current practice often uses the three-parameter functional form

$$\boxed{k(T) = AT^b \exp\left(-\frac{E_A}{R_0 T}\right)}$$

Where A, b and E_A are the three empirical parameters.

Example

Determine the collision theory steric factor for the reaction

$$O+H_2 \rightarrow OH+H$$

At 2000 K given the hard sphere diameters $\sigma_O = 3.050$ and $\sigma_{H_2} = 2.827$Å and the experimental parameters given in the table below.

Reaction	A $((cm^3/gmol)^{n-1}/s)^a$	b	E_A (kJ/gmol)	Temperature Range (K)
$H + O_2 \rightarrow OH + O$	$1.2 \cdot 10^{17}$	−0.91	69.1	300–2500
$OH + O \rightarrow O_2 + H$	$1.8 \cdot 10^{13}$	0	0	300–2500
$O + H_2 \rightarrow OH + H$	$1.5 \cdot 10^{7}$	2.0	31.6	300–2500
$OH + H_2 \rightarrow H_2O + H$	$1.5 \cdot 10^{8}$	1.6	13.8	300–2500
$H + H_2O \rightarrow OH + H_2$	$4.6 \cdot 10^{8}$	1.6	77.7	300–2500
$O + H_2O \rightarrow OH + OH$	$1.5 \cdot 10^{10}$	1.14	72.2	300–2500
$H + H + M \rightarrow H_2 + M$				
$M = Ar$ (low P)	$6.4 \cdot 10^{17}$	−1.0	0	300–5000
$M = H_2$ (low P)	$0.7 \cdot 10^{16}$	−0.6	0	100–5000
$H_2 + M \rightarrow H + H + M$				
$M = Ar$ (low P)	$2.2 \cdot 10^{14}$	0	402	2500–8000
$M = H_2$ (low P)	$8.8 \cdot 10^{14}$	0	402	2500–8000
$H + OH + M \rightarrow H_2O + M$				
$M = H_2O$ (low P)	$1.4 \cdot 10^{23}$	−2.0	0	1000–3000
$H_2O + M \rightarrow H + OH + M$				
$M = H_2O$ (low P)	$1.6 \cdot 10^{17}$	0	478	2000–5000
$O + O + M \rightarrow O_2 + M$				
$M = Ar$ (low P)	$1.0 \cdot 10^{17}$	−1.0	0	300–5000
$O_2 + M \rightarrow O + O + M$				
$M = Ar$ (low P)	$1.2 \cdot 10^{14}$	0	451	2000–10,000

Solution

Equating the collision theory rate coefficient with the three parameter experimental rate coefficient, we have

$$k(T) = pN_{AV}\sigma_{AB}^2\left[\frac{8\pi k_B T}{\mu}\right]^{\frac{1}{2}}\exp\left[-\frac{E_A}{R_0 T}\right] = AT^b\exp\left(-\frac{E_A}{R_0 T}\right)$$

Here we assume the activation energy E_A is the same for both expressions. Solving for steric factor, p, is straightforward, but note the unit

$$p = \frac{AT^b}{N_{AV}\left(\frac{8\pi k_B T}{\mu}\right)^{1/2}\sigma_{AB}^2}$$

We employ

$$A = 1.5\cdot 10^7\ \mathrm{m\ cm^3/gmol-s\ (Table)}$$

$$\mathrm{b} = 2.0(\mathrm{Table}\ 4)$$

$$\sigma_{\mathrm{AB}} = (\sigma_0 + \sigma_{H_2})/2 = (3.050 + 2.827)/2$$

$$= 2.939\ \overset{0}{\mathrm{A}} = 2.939\cdot 10^{-8}\,cm$$

Solution

$$m_0 = \frac{16\text{g/gmol}}{6.022 \cdot 10^{23}\,\text{molecules/gmol}} = 2.66 \cdot 10^{-23}\,g$$

$$m_{H_2} = \frac{2.008}{6.022 \cdot 10^{23}} = 0.332 \cdot 10^{-23}\,g$$

$$\mu = \frac{m_0 m_{H_2}}{m_0 + m_{H_2}} = \frac{2.66(0.332)}{2.66 + 0.332} \cdot 10^{-23} = 2.95 \cdot 10^{-24}\,g$$

$$k_B = 1.381 \cdot 10^{-23}\,\text{J/K} = 1.381 \cdot 10^{-16}\,g.cm^2.s^{-2}.K^{-1}$$

Note: $1\ J/K \equiv 1\ N.m/K \equiv 1\ kg.(m/s^2)\,m/K \equiv 10^3 g.100^2\ cm^2/(s^2K) = 10^7 g.cm^2.s^{-2}.K^{-1}$

$$p = \frac{1.5 \cdot 10^7 (2000)^2}{6.022 \cdot 10^{23} \left(\frac{8\pi(1.381 \cdot 10^{-16})2000}{2.95 \cdot 10^{-24}}\right)^{1/2} (2.939 \cdot 10^{-8})^2}$$

$$= 0.075.$$

Solution

Unit check:

$$p[=]\frac{\mathrm{cm}^3}{\mathrm{gmol}-\mathrm{s}}\frac{1}{\frac{1}{\mathrm{gmol}}\left(\frac{\mathrm{g}-\mathrm{cm}^2}{\mathrm{s}^2-\mathrm{K}}\frac{\mathrm{K}}{\mathrm{g}}\right)^{1/2}\mathrm{cm}^2}=1$$

$$p=0.075(\text{dimension less}).$$

Comments:

- The value of p=0.075 is less than unity as expected. it's small value points out the shortcoming of the simple theory.
- Note that CGS units were employed and not the use of the Avogadro number to calculate the species mass in grams.
- Note that all the units for k(T) are in the pre-exponential factor A; thus the factor T^b is dimensionless as defined.

Other elementary reactions

Unimolecular reactions

Unimolecular reactions involves a single species undergoing a rearrangement to form one or two product species (isomerisation or decomposition).

$$A \rightarrow B \qquad \text{or} \qquad A \rightarrow B + \mathrm{C}$$

Examples of unimolecular reactions include the typical dissociation reactions important to combustion, e.g. $O_2 \rightarrow O + O, H_2 \rightarrow H + H$

Unimolecular reactions are first order at high pressure.

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k_{uni}[\mathrm{A}]$$

Where at low pressure, the reaction rate also depends on the concentration of any molecules, M, with which the reacting species may collide:

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k[\mathrm{A}][\mathrm{M}]$$

A three step mechanism can be used to explain the interesting behaviour. This is to be discussed later.

Other elementary reactions

Termolecular reactions

Termolecular reactions involve three reactant species and correspond to the reverse of the unimolecular reaction at low pressure. A general form is

$$A+B+M \rightarrow C+M$$

Recombination reaction such as $H+H+M \rightarrow H_2+M$ and $H+OH+M \rightarrow H_2O+M$ are important examples of termolecular reactions in combustion.

Termolecular reactions are third order, and their rates can be expressed as

$$\frac{d[A]}{dt} = -k_{ter}[A][B][M],$$

Here M can be any molecule and often referred to as a **third body**. In a radical-radical reaction, a third body is required to carry away the energy generated in forming the stable species. The internal energy of the newly formed molecules is transferred to the third body as kinetic energy of M. without the energy transfer, the newly formed molecule would dissociate back to atoms.

Note: when A and B are the same, a factor of two must multiply the right hand side of the above equation since two A disappear to form C.

Rates of reaction for multistep mechanisms

Net production rates

A sequence of elementary reactions that leads from reactants to products – the **reaction mechanism**.

Mathematically express the net rates for production or destruction for any species participating in a series of elementary steps.

For example, in H_2-O_2 reaction mechanism, (incompletely) given by the following 4 reactions, include both forward and reverse reactions.

$$H_2 + O_2 \underset{k_{f1},k_{r1}}{\Longleftrightarrow} HO_2 + H \qquad \text{(R.1)}$$

$$H + O_2 \underset{k_{f2},k_{r2}}{\Longleftrightarrow} OH + O \qquad \text{(R.2)}$$

$$OH + H_2 \underset{k_{f3},k_{r3}}{\Longleftrightarrow} H_2O + H \qquad \text{(R.3)}$$

$$H + O_2 + M \underset{k_{f4},k_{r4}}{\Longleftrightarrow} HO_2 + M \qquad \text{(R.4)}$$

$$\vdots$$

Where k_{fi} and k_{ri} are the elementary forward and reverse rate coefficients, respectively for the ith reaction.

Rates of reaction for multistep mechanisms

The net rate of production of O_2, is the sum of all the individual elementary rates producing O_2 (reaction R.1, R.2, R.3 reverse) minus the sum of all the rates destroying O_2 (reaction R.1, R.2, R.3 forward)

$$\frac{d[O_2]}{dt} = k_{r1}[HO_2][H] + k_{r2}[OH][O]$$
$$+ k_{r4}[HO_2][M] + \ldots$$
$$- k_{f1}[H_2][O_2] - k_{f2}[H][O_2]$$
$$- k_{f4}[H][O_2][M] - \ldots$$

Similarly, for H atoms

$$\frac{d[H]}{dt} = k_{f1}[H_2][O_2] + k_{r2}[OH][O]$$
$$+ k_{f3}[\overset{OH}{\cancel{HO_2}}][H_2] + k_{r4}[HO_2][M] + \ldots$$
$$- k_{r1}[HO_2][H] - k_{f2}[H][O_2]$$
$$- k_{r3}[H_2O][H] - k_{f4}[H][O_2][M] - \ldots$$

Rates of reaction for multistep mechanisms

We can write similar expressions for each species participating in the mechanism, which yields a system of first-order ordinary differential equations that describes the evolution of the chemical system starting from given initial conditions

$$\frac{\mathrm{d}[X_i](t)}{\mathrm{d}t} = f_i([X_1](t),[X_2](t),\cdots,[X_n](t))$$

With initial condition as

$$[X_i](0) = [X_i]_0$$

This set of equations for a particular system, coupled with mass, momentum, or energy conservations, and state equations, can be numerically integrated.

Packaged routines can efficiently integrate **stiff** systems.

A set of equations is considered stiff when one or more variables change very rapidly while others change very slowly. This is disparity in time scales is common in chemical systems where radical reactions are fast compared with reactions involving stable species.

Compact notation

A compact notation has been developed to represent both the mechanism and the individual species production rates. For the mechanism, we can write

$$\sum_{j=1}^{N} v'_{ji} X_j \Leftrightarrow \sum_{j=1}^{N} v''_{ji} X_j \quad \text{for } i = 1,2,\ldots,L,$$

reactant products

Where v'_{ji} and v''_{ji} are the stoichiometric coefficients on the reactants and products side of the equation, respectively, for the jth species in the ith reaction.

For example, for the reaction R.1-R.4, involving 8 species O_2, H_2, H_2O, O, H, OH, and M. Define j and i as

j	Species	i	Reaction
1	O_2	1	R.1
2	H_2	2	R.2
3	H_2O	3	R.3
4	HO_2	4	R.4
5	O		
6	H		
7	OH		
8	M		

Compact notation

Using j as the column index and i the row index, we can write the stoichiometric coefficient matrices as

$$\nu'_{ji} = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \end{bmatrix} \qquad \nu''_{ji} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$H_2 + O_2 \underset{k_{f1},k_{r1}}{\Longleftrightarrow} HO_2 + H \qquad \text{(R.1)}$$

$$H + O_2 \underset{k_{f2},k_{r2}}{\Longleftrightarrow} OH + O \qquad \text{(R.2)}$$

$$OH + H_2 \underset{k_{f3},k_{r3}}{\Longleftrightarrow} H_2O + H \qquad \text{(R.3)}$$

$$H + O_2 + M \underset{k_{f4},k_{r4}}{\Longleftrightarrow} HO_2 + M \qquad \text{(R.4)}$$

$$\vdots$$

j	Species	i	Reaction
1	O_2	1	R.1
2	H_2	2	R.2
3	H_2O	3	R.3
4	HO_2	4	R.4
5	O		
6	H		
7	OH		
8	M		

Rates of reaction for multistep mechanisms

Compact notation

As elementary reactions involve at most 3 reactant species, the coefficient matrices will always be sparse when large number of species are involved.

The following three relationships compactly express the net production rate of each species in a multistep mechanism

$$\dot{\omega}_j = \sum_{i=1}^{L} v_{ji} \quad \text{for} \quad i = 1,2,\dots,L$$

Where $$v_{ji} = v''_{ji} - v'_{ji}$$

And $$q_i = k_{fi} \prod_{j=1}^{N} [X_J]^{v'_{ji}} - k_{ri} \prod_{j=1}^{N} [X_J]^{v''_{ji}}$$

$\dot{\omega}_j$ is the production rates. For systems in which the species concentrations are only affected by chemical transformations $\dot{\omega}_j \equiv d[X_J]/dt$ for the complete mechanism.

Rates of reaction for multistep mechanisms

Compact notation

q_i, the **rate-of-progress variable** for the ith elementary reaction was defined.

The symbol $\prod$ is used to denote a product of items(similar as $\sum$). For example for reaction R.1, $q_i(= q_1)$ is expressed

$$
\begin{aligned}
q_i &= k_{f1}[\mathrm{O_2}]^1[\mathrm{H_2}]^1[\mathrm{H_2O}]^0[\mathrm{HO_2}]^0[\mathrm{O}]^0[\mathrm{H}]^0[\mathrm{OH}]^0[\mathrm{M}]^0 \\
&\quad - k_{r1}[\mathrm{O_2}]^0[\mathrm{H_2}]^0[\mathrm{H_2O}]^0[\mathrm{HO_2}]^1[\mathrm{O}]^0[\mathrm{H}]^1[\mathrm{OH}]^0[\mathrm{M}]^0 \\
&= k_{f1}[\mathrm{O_2}][\mathrm{H_2}] - k_{r1}[\mathrm{HO_2}][\mathrm{H}].
\end{aligned}
$$

$$H_2 + O_2 \underset{k_{f1},k_{r1}}{\Longleftrightarrow} HO_2 + H \qquad \text{(R.1)}$$

Write similar expression for i=2, 3, 4, taking into account whether the jth species is created, destroyed or not participated, complete the total rate expression for $\dot{\omega}_j$.

The compact notation is particularly useful when solving chemical kinetic problems using computer. Computer programmes such as CHEMKIN is a widely used package for solving chemical kinetic problems. `

Relation between rate coefficients and equilibrium constants

Measuring rate coefficients of elementary reactions is a difficult task with a large degree of uncertainties. Reliable rate coefficients often are known no better than within a factor of 2, others may be uncertain by an order of magnitude or more.

Equilibrium constants however are based on thermodynamic measurements or calculation, therefore are very accurate.

At equilibrium, the forward and reverse reaction rates must be equal.

Consider an reaction

$$A + B \underset{k_f, k_r}{\Longleftrightarrow} C + D$$

For species A, we have

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_f[\mathrm{A}][\mathrm{B}] + k_r[\mathrm{C}][\mathrm{D}]$$

At equilibrium, the time rate of change of [A] must be zero, so we have

$$0 = -k_f[\mathrm{A}][\mathrm{B}] + k_r[\mathrm{C}][\mathrm{D}]$$

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Relation between rate coefficients and equilibrium constants

Rearranging, we have

$$\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} = \frac{k_f(T)}{k_r(T)}$$

In Thermochemistry, we defined the equilibrium constant based on partial pressures for an arbitrary equilibrium reaction to be

$$K_p = \frac{\left(\frac{p_C}{p^0}\right)^c \left(\frac{p_D}{p^0}\right)^d \ldots}{\left(\frac{p_A}{p^0}\right)^a \left(\frac{p_B}{p^0}\right)^b \ldots}$$

product

reactant

Where the superscripts are the stoichiometric coefficients, i.e. $v_i' = a, b, \ldots$ and $v_i'' = c, d, \ldots$.

The molar concentration relate to the mole fractions and partial pressure as

$$[X_i] = \frac{\chi_i p}{R_0 T} = \frac{p_i}{R_0 T}$$

Relation between rate coefficients and equilibrium constants

We can define an equilibrium constant based on molar concentrations, K_c

$$K_c = \frac{[C]^c[D]^d \ldots}{[A]^a[B]^b \ldots} = \frac{\prod_{prod}[X_i]^{v_i''}}{\prod_{reac}[X_i]^{v_i'}} = \left(\frac{p_0}{RT}\right)^{\sum_{prod}-\sum_{reac}} \cdot \frac{\prod_{prod} X}{\prod_{reac}}$$

why ?

So we have

$$K_p = K_c\left(\frac{R_oT}{p^0}\right)^{c+d+\cdots-a-b-\cdots}$$

Or

$$K_p = K_c\left(\frac{R_oT}{p^0}\right)^{\sum v''-\sum v'}$$

From this, we have the ratio of the forward and reverse rate coefficients equals the equilibrium constant K_c

In equilibrium $k_r[T][C]^c[D]^d = k_f[T][A]^a[B]^b$

$$K_c = \frac{[C]^c[D]^d \ldots}{[A]^a[B]^b \ldots} = \frac{\prod_{prod}[X_i]^{v_i''}}{\prod_{reac}[X_i]^{v_i'}} = \frac{k_f[T]}{k_r[T]}$$

Constant

Rates of reaction for multistep mechanisms

Relation between rate coefficients and equilibrium constants

$$K_c = \frac{k_f[T]}{k_r[T]}$$

For bimolecular reactions, we have $K_c = K_p$

From the above equation, we can compute a reverse reaction rate from a knowledge of the forward rate and the equilibrium constant of the reaction; or vise versa, if we know the reverse rates, we can calculate the forward rates.

These rates are temperature dependant. Over a wide temperature range, different choices may have to be made.

The National Institute of Standards and Technology maintains a database providing rate information on well over 6000 reactions.

Example

In the following reaction, the forward rate is recommended.

$$NO + O \Leftrightarrow N + O_2$$

$$k_f = 3.80 \times 10^9\, T^{1.0} \exp\left(-\frac{20{,}820}{T}\right) [=] \frac{cm^3}{gmol.s}$$

Determine the rate coefficient k_r for the reverse reaction at 2300 K.

Solution

The forward and reverse rate coefficients are related to the equilibrium constant K_p

$$\frac{k_f(T)}{k_r(T)} = K_c(T) = K_p(T)$$

Therefore to evaluate k_r we need to find out k_f and K_p at 2300 K. We know

$$K_p = \exp\left(-\frac{\Delta G_T^0}{R_0 T}\right)$$

Where $\Delta G_{2300\,K}^0 = \left[\bar{g}_{f,N}^0 + \bar{g}_{f,O_2}^0 - \bar{g}_{f,NO}^0 - \bar{g}_{f,O}^0\right]_{2300\,K}$

$$= 326{,}331 + 0 - 61{,}243 - 101{,}627 = 163{,}461\ kJ/kmol$$

$$K_p = \exp\left(-\frac{163{,}461}{8.315\ \times 2300}\right) = 1.94 \times 10^{-4}\ (dimensionless)$$

The forward rate is

$$k_f = 3.8 \times 10^9 (2300) \exp\left(-\frac{20{,}820}{2300}\right) = 1.024 \times 10^9 \frac{cm^3}{gmol.s}$$

So

$$k_r = \frac{k_f}{K_p} = \frac{1.024 \times 10^9}{1.94 \times 10^{-4}} = 5.28 \times 10^{12}\ \frac{cm^3}{gmol.s}$$

Steady state approximation

- In many combustion related reactions, highly reactive intermediate species, e.g. radical, are formed. Analysis of such systems can sometimes be simplified by applying the **steady state approximation** to the reactive intermediate radicals.
- Physically, after a rapid initial buildup in concentration, the radical is destroyed as rapidly as it is formed (same formation rate and destruction rate). The concentration of radicals are usually small in comparison with those of the reactants and products.
- We use the Zeldovich mechanism for the formation of nitric oxide as an example:

$$O + N_2 \xrightarrow{k_1} NO + N$$
$$N + O_2 \xrightarrow{k_2} NO + O$$

The first reaction is slow and the second is extremely fast. The net product rate of N atoms is

$$\frac{d(N)}{dt} = k_1[O][N_2] - k_2[N][O_2]$$

Steady state approximation

$$\frac{d(N)}{dt} = k_1[O][N_2] - k_2[N][O_2]$$

- After a rapid transient allowing the buildup of N atoms to a low concentration, the two terms of lift side of the above equation become equal, therefore $\frac{d(N)}{dt}$ becomes zero. Hence we can determine the steady state concentration of N atoms as:

why?

$$0 = k_1[O][N_2] - k_2[N]_{ss}[O_2]$$

Rearrange

$$[N]_{ss} = \frac{k_1[O][N_2]}{k_2[O_2]}$$

- Although we assume $[N]_{ss}$ does not change with time, it may still change as it rapidly re-adjusts according to the above equation. We can determine the time rate-of-change by

$$\frac{d[N]_{ss}}{dt} = \frac{d}{dt}\left[\frac{k_1[O][N_2]}{k_2[O_2]}\right]$$

We will apply this approximation to the unimolecular reactions in the next part.

The mechanism for unimolecular reactions

We previously discussed the unimolecular reactions without considering the pressure dependence.

To explain the pressure dependence requires a three-step mechanism

$$A + M \xrightarrow{k_e} A^* + M \qquad \text{(S1)}$$

energised

$$A^* + M \xrightarrow{k_{de}} A + M \qquad \text{(S2)}$$

denergised

$$A^* \xrightarrow{k_{uni}} products. \qquad \text{(S3)}$$

unimolecular

In the first step (S1), molecule A collides with the "third body" M and receives kinetic energy from M. A is transformed to A* as *energised A*. Two things can happen to A*:

1. It collides with a "third body" and losses kinetic energy, thus converting back to A.
2. It fly apart in a true unimolecular process and form products.

The mechanism for unimolecular reactions

To observe the pressure dependence, we can write an expression to describe the rate of products formation

$$\frac{d[products]}{dt} = k_{uni}[A^*]$$

To evaluate $[A^*]$, we employ the steady state approximation. The net production of A* can be expressed as

$$\frac{d[A^*]}{dt} = k_e[A][M] - k_{de}[A^*][M] - k_{uni}[A^*]$$

If we assume $\frac{d[A^*]}{dt} = 0$, i.e. steady state after initial rapid transient, we have

$$[A^*] = \frac{k_e[A][M]}{k_{de}[M] + k_{uni}}$$

Substituting this into the above equation, we have

$$\frac{d[products]}{dt} = \frac{k_{uni}k_e[A][M]}{k_{de}[M] + k_{uni}} = \frac{k_e[A][M]}{(\frac{k_{de}}{k_{uni}})[M] + 1}$$

The mechanism for unimolecular reactions

For the overall reaction,

$$A \xrightarrow{k_{app}} products$$

$$= \frac{k_e[A][M]}{(\frac{k_{de}}{k_{uni}})[M]+1}$$

We can write

$$-\frac{d[A]}{dt} = \frac{d[products]}{dt} = k_{app}[A]$$

apparent

Where k_{app} is defined as apparent unimolecular rate coefficient. Then we have

$$k_{app} = \frac{k_e[M]}{(\frac{k_{de}}{k_{uni}})[M] + 1}$$

This equation can help us to understand the pressure dependence of unimolecular reactions.

- When pressure increases, [M] (kmol/m^3) increases. At high enough pressure, $(\frac{k_{de}}{k_{uni}})[M]$ becomes much larger than 1, and [M] can cancel, thus

  $p\uparrow \rightarrow M\uparrow$

$$k_{app}(p \rightarrow \infty) = k_{uni}k_e/k_{de}$$

- At low enough pressure, $(\frac{k_{de}}{k_{uni}})[M]$ is much less than 1, hence

$$k_{app}(p \rightarrow 0) = k_e[M]$$

Chain and chain-branching reactions

- **Chain reactions** involve the production of a radical species that subsequently reacts to produce another radical; this radical reacts to produce another radical.
- The sequence of events, or chain reaction, continues until a reaction involving the formation of a stable species.
- Chain reactions can occur in many chemical processes of importance to combustion.
- Now we have a hypothetical chain mechanism as follows:

$$A_2 + B_2 \rightarrow 2AB$$

The **chain-initiation reaction** is

$$A_2 + M \xrightarrow{k_1} A + A + M \qquad \text{(C1)}$$

The **chain-propagating reactions** involving the free radicals A and B are

$$A + B_2 \xrightarrow{k_2} AB + B \qquad \text{(C2)}$$

$$B + A_2 \xrightarrow{k_3} AB + A \qquad \text{(C3)}$$

the **chain-terminating reaction** is

$$A + B + M \xrightarrow{k_4} AB + M \qquad \text{(C4)}$$

Chain and chain-branching reactions

In the early stages of reaction, the concentration of the product AB is small, the same for A and B. therefore we can neglect the reverse reactions to determine the reaction rates for the stable species at this stage

$$\frac{d[A_2]}{dt} = -k_1[A_2][M] - k_3[B][A_2]$$

$$\frac{d[B_2]}{dt} = -k_2[B_2][A]$$

$$\frac{d[AB]}{dt} = k_2[A][B_2] + k_3[B][A_2] + k_4[A][B][M]$$

For the radicals A and B, we invoke the steady-state approximation

$$2k_1[A_2][M] - k_2[B_2][A] + k_3[B][A_2] - k_4[A][B][M] = 0 \qquad \frac{d[A]}{dt}$$

And $$k_2[B_2][A] - k_3[B][A_2] - k_4[A][B][M] = 0 \qquad \frac{d[B]}{dt}$$

Solving the above two equations simultaneously for [A], we have

$$[\mathrm{A}] = \frac{k_1}{2k_2}\frac{[\mathrm{M}][\mathrm{A}_2]}{[\mathrm{B}_2]} + \frac{k_3}{k_4}\frac{[\mathrm{A}_2]}{[\mathrm{M}]}\left\{\left[1 + \left(\frac{k_1 k_4}{2k_2 k_3}\frac{[\mathrm{M}]^2}{[\mathrm{B}_2]}\right)^2\right]^{1/2} - 1\right\}$$

Similarly, a complicated expression for [B] can be found. After we know the steady-state values for [A] and [B], the initial reactions rates for A_2, B_2 and AB can be determined. B_2 is the simplest because it appears only once:

$$\frac{\mathrm{d}[B_2]}{\mathrm{d}t} = -\frac{k_1}{2}[\mathrm{M}][\mathrm{A}_2] - \frac{k_2 k_3}{k_4}\frac{[\mathrm{A}_2][\mathrm{B}_2]}{[\mathrm{M}]}\left\{\left[1+\left(\frac{k_1 k_4}{2k_2 k_3}\frac{[\mathrm{M}]^2}{[\mathrm{B}_2]}\right)^2\right]^{1/2} - 1\right\}$$

The equations concerns [A] and $\frac{d[B_2]}{dt}$ can be simplified by recognising that in the second term, $\frac{k_1 k_4 [M]^2}{2k_2 k_3 [B_2]} \ll 1$. This is because the rate coefficients for the radical reactions, k_2 and k_3, are much larger than k_1 and k_4 for the steady-state approximation to apply. Using a truncated Taylor series, we have

$(1+x)^a = 1 + ax + \frac{a(a-1)}{2}x^2 + \cdots$

$$[\mathrm{A}] \approx \frac{k_1}{2k_2}\frac{[\mathrm{A}_2][\mathrm{M}]}{[\mathrm{B}_2]} + \frac{k_1^2 k_4}{8k_2^2 k_3}\frac{[\mathrm{A}_2][\mathrm{M}]^3}{[\mathrm{B}_2]^2}$$

And

$$\frac{\mathrm{d}[\mathrm{B}_2]}{\mathrm{d}t} \approx -\frac{k_1}{2}[\mathrm{A}_2][\mathrm{M}] - \frac{k_1^2 k_4}{4k_2 k_3}\frac{[\mathrm{A}_2][\mathrm{M}]^3}{[\mathrm{B}_2]}.$$

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Comments

k_1 k_2

- A simple order-of-magnitude analysis shows that the first term in both equations above dominates at low pressures; thus the concentration of A depends directly on the ratio of the C.1 (initiation step) rate coefficient to the C.2 (first propagation step) rate coefficient, and the rate of B_2 disappearing is governed only by C.1.
- Note k_2 and k_3 are not in the above equations, meaning increasing them has no effect on the production rate of the products, although increase the rate coefficients of the chain-propagating steps would increase the radical concentrations. Radical concentrations are proportional to pressure, and the reaction rates of the major species scale with the pressure squared.
- C.4 (termolecular chain-terminating step) rate coefficient k_4 has no effect on either the radical concentrations or the overall reaction rate; however at high pressure k_4 has an influence, which is reflected in the second terms in above equations, and the effect becomes important at high pressures. Note: the molar concentration ($kmol/m^3$) scales directly with pressure when mole fraction and temperature are fixed.

Chain-branching reactions

- Chain branching reactions involve the formation of two radical species from a reaction that consumes only one radical.
- For instance, reaction $O + H_2O \rightarrow OH + OH$ is a chain branching reaction.
- The existence of a chain-branching step in a chain mechanism can have an explosive effect.
- In a system with chain branching, it is possible for the concentration of a radical species to build up geometrically, causing the rapid formation of products. In this case, the rate of chain-initiation step does not control the overall reaction rate.
- With chain branching, the rates of radical reaction dominate.
- Chain branching reactions are responsible for a flame being self propagating and are an essential ingredient in combustion chemistry.

Example

A famous chain mechanism is the Zeldovich, or thermal mechanism for the formation of nitric oxide from atmospheric nitrogen.

$$N_2 + O \xrightarrow{k_{1f}} NO + N$$

$$N + O_2 \xrightarrow{k_{2f}} NO + O$$

Because the second reaction is much faster than the first, the steady-state approximation can be used to evaluate the N-atom concentration. Furthermore, in high-temperature systems, the NO formation reaction is typically much slower than other reactions involving O_2 and O. Thus O_2 and O can be assumed to be in equilibrium:

why

$$O_2 \overset{K_p}{\Leftrightarrow} 2O$$

Construct a global mechanism

$$N_2 + O_2 \xrightarrow{k_G} 2NO$$

Represented as

$$\frac{d[NO]}{dt} = k_G[N_2]^m[O_2]^n$$

Determine k_G, m and n using the elementary rate coefficient, etc., from the detailed mechanism.

Solution

From the elementary reactions, we have

$$\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t} = k_{1f}[\mathrm{N_2}][\mathrm{O}] + k_{2f}[\mathrm{N}][\mathrm{O_2}]$$

$$\frac{\mathrm{d}[\mathrm{N}]}{\mathrm{d}t} = k_{1f}[\mathrm{N_2}][\mathrm{O}] - k_{2f}[\mathrm{N}][\mathrm{O_2}]$$

Here we assume reverse rates are negligible.

With the steady-state approximation, we have $\frac{d[N]}{dt} = 0$, thus

$$[\mathrm{N}]_{ss} = \frac{k_{1f}[\mathrm{N_2}][\mathrm{O}]}{k_{2f}[\mathrm{O_2}]}$$

Sub this in the first equation, we have

$$\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t} = k_{1f}[\mathrm{N_2}][\mathrm{O}] + k_{2f}[\mathrm{O_2}]\left(\frac{k_{1f}[\mathrm{N_2}][\mathrm{O}]}{k_{2f}[\mathrm{O_2}]}\right) = 2k_{1f}[\mathrm{N_2}][\mathrm{O}]$$

Solution

We now eliminate [O] through our equilibrium approximation

PV=nRT

$$K_p = \frac{p_O^2}{p_{O_2} p^0} = \frac{[O]^2 (R_0 T)^2}{[O_2](R_o T) p^0} = \frac{[O]^2}{[O_2]} \frac{R_0 T}{p^0}$$

$O_2 \rightleftharpoons 2O$

$$\frac{\left(\frac{P_O}{P^0}\right)^2}{\frac{P_{O_2}}{P^0}}$$

Re-arrange

$$[O] = \left[[O_2] \frac{K_p p^0}{R_0 T} \right]^{1/2}$$

$2k_{1f}[N_2][O]$

thus

$$\frac{d[NO]}{dt} = 2k_{1f} \left(\frac{K_p p^0}{R_0 T} \right)^{1/2} [N_2][O_2]^{1/2}$$

From this, we can identify the global parameters:

$N_2 + O_2 = 2NO$

$$\boxed{\begin{aligned} k_G &= 2k_{1f} \left(\frac{K_p p^0}{R_0 T} \right)^{1/2} \\ m &= 1 \\ n &= 1/2 \end{aligned}}$$

initial reaction only

Example

Consider the shock-heating of air to 2500 K, 3 atm. Use the results from last example, determine:

1. The initial nitric oxide formation rate in ppm/s
2. The amount of nitric oxide formed (in ppm) in 0.25ms

The rate coefficient, k_{1f}, is

$$k_{1f} = 1.82 \times 10^{14} \exp\left[-\frac{38{,}370}{T(K)}\right] \frac{cm^3}{gmol.s}$$

Solution

1. Find $\frac{d\chi_{NO}}{dt}$, we can evaluate $d[NO]/dt$ from

$$\frac{d[NO]}{dt} = 2k_{1f}\left(\frac{K_p p^0}{R_0 T}\right)^{1/2}[N_2][O_2]^{1/2}$$

Where we assume

$$\chi_{N_2} \cong 0.79$$
$$\chi_{O_2} \cong 0.21$$

Since χ_{NO} and χ_O are both quite small and can be neglected in estimating χ_{N_2} and χ_{O_2}.

p = 3atm

We can convert the mole fraction to molar concentration using

$$[N_2] = \chi_{N_2}\frac{p}{R_0 T} = 0.79\frac{3(101{,}325)}{8315(2500)} = 1.155 \times 10^{-2}\ kmol/m^3$$

$$[O_2] = \chi_{O_2}\frac{p}{R_0 T} = 0.21\frac{3(101{,}325)}{8315(2500)} = 3.071 \times 10^{-3}\ kmol/m^3$$

Solution

Evaluate the rate coefficient

$$k_{1f} = 1.82 \times 10^{14} \exp\left[-\frac{38{,}370}{2500}\right] = 3.93 \times 10^{7} \frac{cm^3}{gmol.s} = 3.93 \times 10^{4} \frac{m^3}{kmol.s}$$

To find the equilibrium constant, we employ the Gibbs function

$$\Delta G_T^0 = \left[(2)\bar{g}_{f,O}^0 - (1)\bar{g}_{f,O_2}^0\right]_{2500\,K}$$
$$= 2(88{,}203) - 1(0) = 176{,}406\ kJ/kmol \qquad \text{(from property table)}$$

$$K_p = \frac{p_O^2}{p_{O_2} p^0} = \exp\left(-\frac{\Delta G_T^0}{R_0 T}\right)$$

$$K_p p^0 = \exp\left(-\frac{\Delta G_T^0}{R_0 T}\right) p^0 = \exp\left(-\frac{176{,}406}{8.315(2500)}\right) 1\ atm = 2.063 \times 10^{-4}\ atm = 20.90\ Pa$$

We can now evaluate $d[NO]/dt$ $= 2k_{1f}\left(\frac{K_p p^0}{R_0 T}\right)^{\frac{1}{2}} \cdot [N_2][O_2]^{\frac{1}{2}}$

$$\frac{d[NO]}{dt} = 2(3.93 \times 10^4)\left(\frac{20.90}{8314 \times 2500}\right)^{1/2} 1.155 \times 10^{-2}(3.071 \times 10^{-3})^{1/2} = 0.0505 \frac{kmol}{m^3 s}$$

Or in ppm

$$\frac{d\chi_{NO}}{dt} = \frac{R_0 T}{\underbrace{p}_{PV=nRT}} \frac{d[NO]}{dt} = \frac{8315(2500)}{3(101{,}325)} 0.0505 = \frac{3.45\ kmol/kmol}{s} = 3.45 \times 10^6\ ppm/s$$

Solution

2. Find $\chi_{NO}(t = 0.25\ ms)$. If we assume that the N_2 and O_2 concentrations do not change with time and that reverse reactions are unimportant over the 0.25 ms interval, we can simply integrate d[NO]/dt

$$\int_0^{[NO](t)} d[NO] = \int_0^t k_G[N_2][O_2]^{1/2} dt$$

We have

$$[NO](t) = k_G[N_2][O_2]^{\frac{1}{2}} t = 0.0505(0.25 \times 10^{-3})$$
$$= 1.263 \times 10^{-5}\ kmol/m^3$$

Or

$$\chi_{NO} = [NO]\frac{R_0 T}{p}$$
$$= 1.263 \times 10^{-5}\left(\frac{8315(2500)}{3(101{,}325)}\right) = 8.64 \times 10^{-4} kmol/kmol$$
$$\chi_{NO} = 864\ ppm$$

Unimolecular reactions

In analysing combustion processes, insight can be gained from a knowledge of chemical time scales.

Consider the unimolecular reaction we discussed before, and the corresponding reaction rate expression.

$$A \xrightarrow{k_{app}} products$$

$$-\frac{d[A]}{dt} = \frac{d[products]}{dt} = k_{app}[A]$$

$$\frac{d[A]}{[A]} = -k_{app}dt$$

The reaction rate can be integrated, assuming constant temperature to yield the time history of [A]

$$[A](t) = [A]_0 \exp(-k_{app}t)$$

Where $[A]_0$ is the initial concentration of species A.

Unimolecular reactions

We define a characteristic time, or time constant, similar as a simple resister-capacitor electrical network, τ_{chem}, to be the time required for the concentration of A to fall from its initial value a value equal to $1/e$ times the initial value

$e^{-k_{app}\tau_{chem}} = e^{-1}$

$$\frac{[A](\tau_{chem})}{[A]_0} = \exp(-k_{app}\tau_{chem}) = 1/e$$

So we have

$$\tau_{chem} = 1/k_{app}$$

This equation shows that to estimate the time scale of simple unimolecular reactions all that is required is the apparent rate coefficient k_{app}

Bimolecular reactions

Now consider a bimolecular reaction

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

And the rate expression is

$$\frac{d[A]}{dt} = -k_{bimolec}[A][B]$$

For this single reaction taking place in the absence of other reactions, the concentration of A and B are related simply through stoichiometry. For every mole of A destroyed, one mole of B destroyed too. So any change in [A] has a corresponding change in [B]

$$x \equiv [A]_0 - [A] = [B]_0 - [B]$$

So the concentration of B is related to the concentration of A as

$$[B] = [B]_0 + [A] - [A]_0$$

Substituting the x equation to the rate expression, and integrate we have

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Bimolecular reactions

$[A](t) = [A]_0 e^{-k_{app} \cdot t}$

$$\frac{[A](t)}{[B](t)} = \frac{[A]_0}{[B]_0} \exp[([A]_0 - [B]_0) k_{bimolec} t]$$

The concentration of B is related to the concentration of A as

$$[B] = [B]_0 + [A] - [A]_0$$

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Substituting this to above, and setting $\frac{[A]}{[A]_0} = 1/e$ when $t = \tau_{chem}$ to define the characteristic time, we have

$B_0 > A_0$

$$\tau_{chem} = \frac{\ln\left[e + (1-e)\left(\frac{[A]_0}{[B]_0}\right)\right]}{([B]_0 - [A]_0) k_{bimolec}} \qquad (e = 2.718)$$

$\ln(>0)$

$\tau > 0$

Often, one of the reactants is in much grater abundance than the other. In the case when $[B]_0 \gg [A]_0$, the equation is simplified to

$$\tau_{chem} = \frac{1}{[B]_0 k_{bimolec}}$$

$\tau = \frac{1}{k_{app}}$

Termolecular reactions

For a simple termolecular reaction

$$A + B + M \rightarrow C + M$$

Since for a simple system at constant temperature, the third body concentration is constant. The reaction rate expression is mathematically identical to the bimolecular rate expression where $k_{ter}[M]$ replaces $k_{bimolec}$

$$\frac{d[A]}{dt} = -k_{ter}[M][A][B]$$

So the characteristic time for the termolecular reaction is then

$$\tau_{chem} = \frac{\ln\left[e + (1-e)\left(\frac{[A]_0}{[B]_0}\right)\right]}{([B]_0 - [A]_0)k_{ter}[M]}$$

And when $[B]_0 \gg [A]_0$, it becomes

$$\tau_{chem} = \frac{1}{[B]_0 k_{ter}[M]}$$

Example

Consider the flowing combustion reaction

	Reaction	Rate coefficient
i	$CH_4 + OH \rightarrow CH_3 + H_2O$	$k\left(\text{cm}^3/\text{gmol-s}\right) = 1.00 \cdot 10^8 T\left(K\right)^{1.6} \exp\left[-1570/T\left(K\right)\right]$
ii	$CO + OH \rightarrow CO_2 + H$	$k\left(\text{cm}^3/\text{gmol-s}\right) = 4.76 \cdot 10^7 T\left(K\right)^{1.23} \exp\left[-35.2/T\left(K\right)\right]$
iii	$CH + N_2 \rightarrow HCN + N$	$k\left(\text{cm}^3/\text{gmol-s}\right) = 2.86 \cdot 10^8 T\left(K\right)^{1.1} \exp\left[-10267/T\left(K\right)\right]$
iv	$H + OH + M \rightarrow H_2O + M$	$k\left(\text{cm}^6/\text{gmol}^2\text{-s}\right) = 2.20 \cdot 10^{22} T\left(K\right)^{-2.0}$

Reaction i is an important step in the oxidation of CH_4, and reaction ii is the key step in CO oxidation. Reaction iii is a rate limiting step in the prompt-NO mechanism, and reaction iv is a typical radical recombination reaction.

Estimate the characteristic chemical times associated with the least abundant reactant in each of these reactions for the following two conditions.

Example

Condition I (low temperature)

$$T = 1344.3\ K$$

$$p = 1\ atm$$

$$\chi_{CH_4} = 2.012 \times 10^{-4}$$

$$\chi_{N_2} = 0.7125$$

$$\chi_{CO} = 4.083 \times 10^{-3}$$

$$\chi_{OH} = 1.818 \times 10^{-4}$$

$$\chi_{H} = 1.418 \times 10^{-4}$$

$$\chi_{CH} = 2.082 \times 10^{-9}$$

$$\chi_{H_2O} = 0.1864$$

Condition II (high temperature)

$$T = 2199.2\ K$$

$$p = 1\ atm$$

$$\chi_{CH_4} = 3.773 \times 10^{-6}$$

$$\chi_{N_2} = 0.7077$$

$$\chi_{CO} = 1.106 \times 10^{-2}$$

$$\chi_{OH} = 3.678 \times 10^{-3}$$

$$\chi_{H} = 6.634 \times 10^{-4}$$

$$\chi_{CH} = 9.148 \times 10^{-9}$$

$$\chi_{H_2O} = 0.1815$$

Assuming that each of the four reactions is uncoupled from all other reactions and that the third-body collision partner concentration is the sum of the N_2 and H_2O concentration.

Solution

We have reactions i, ii, and iii as bimolecular reactions and reaction iv as termolecular reaction.

For reaction i at condition I, we treat OH as species A and it's mole fraction is slightly lower than that of CH_4. converting the mole fraction to mole concentration, we have

$$[OH] = \chi_{OH}\frac{p}{R_0T} = 1.818\times10^{-4}\frac{101315}{8315(1344.3)}$$

$$= 1.648\times10^{-6}\ kmol/m^3 \text{ or } 1.648\times10^{-9}\ gmol/cm^3$$

$$[CH_4] = \chi_{CH_4}\frac{p}{R_0T} = 2.012\times10^{-4}\frac{101315}{8315(1344.3)}$$

$$= 1.824\times10^{-6}\ kmol/m^3 \text{ or } 1.824\times10^{-9}\ gmol/cm^3$$

Evaluate the rate coefficient,

$$k_1 = 1.00\cdot10^{8}\left(1344.3\right)^{1.6}\exp\left[-1507/1344.3\right]$$

$$= 3.15\cdot10^{12}\ \text{cm}^3/\text{gmol-s}$$

$$[H] = \chi_H\frac{p}{R_0T} = 1.418\times10^{-4}\times10^{-4}\times\frac{101315}{8315(1344.3)} = 1.285\times10^{-6}\ kmol/m^3$$

Solution

Since $[CH_4]$ and $[OH]$ are of the same order of magnitude, we use the equation developed before to evaluate τ_{chem} $\tau_{chem} = \frac{\ln\left(e + (1-e)\frac{[A_0]}{[B_0]}\right)}{[B_0]-[A_0]k_{ter}[M]}$

$$\tau_{OH} = \frac{\ln\left[2.718 - 1.718\left([OH]/[CH_4]\right)\right]}{\left([CH_4]-[OH]\right)k_i}$$

$$= \frac{\ln\left[2.718 - 1.718\left(1.648\cdot 10^{-9}/1.824\cdot 10^{-9}\right)\right]}{\left(1.824\cdot 10^{-9} - 1.648\cdot 10^{-9}\right)3.15\cdot 10^{12}} = \frac{0.1534}{554.4}$$

$$\tau_{OH} = 2.8 \times 10^{-4}\ s \text{ or } 0.28ms$$

For reaction i, ii, iii, because the reactants are at similar order of magnitude, the estimations are computed similarly. For the termolecular reaction iv at condition I

$$[M] = \left(\chi_{N_2} + \chi_{H_2O}\right)\frac{p}{R_0 T} = (0.7125 + 0.1864)\frac{101325}{8315(1344.3)}$$

$$= 8.148 \times 10^{-3}\ kmol/m^3 \text{ or } 8.148 \times 10^{-6}\ gmol/cm^3$$

So

$$\tau_H = \frac{\ln\left[2.718 - 1.718\left(\frac{[H]}{[OH]}\right)\right]}{([OH]-[H])[M]k_{iv}}$$

Solution

$$\tau_{\mathrm{H}} = \frac{\ln\left[2.718 - 1.718\left(1.285\cdot 10^{-9}\right)/\left(1.648\cdot 10^{-9}\right)\right]}{\left(1.648\cdot 10^{-9} - 1.285\cdot 10^{-9}\right)8.149\cdot 10^{-6}\left(1.217\cdot 10^{16}\right)}$$

$$\tau_H = 8.9 \times 10^{-3}\ s \quad or \quad 8.9\ ms$$

Similar calculations are performed for condition II and results are shown below

Condition	Reaction	Species A	$k_i(T)$	τ_A(ms)
I	I	OH	$3.15 \cdot 10^{12}$	0.28
I	Ii	OH	$3.27 \cdot 10^{11}$	0.084
I	Iii	CH	$3.81 \cdot 10^{8}$	0.41
I	Iv	H	$1.22 \cdot 10^{16}$	8.9
II	I	CH_4	$1.09 \cdot 10^{13}$	0.0045
II	Ii	OH	$6.05 \cdot 10^{11}$	0.031
II	Iii	CH	$1.27 \cdot 10^{10}$	0.020
II	iv	H	$4.55 \cdot 10^{15}$	2.3

Partial equilibrium

- Many combustion processes simultaneously involve both fast and slow reactions such that the fast reactions are rapid in both the forward and reverse directions.
- These fast reactions are usually chain-propagating or chain-branching steps, whereas the slow reactions are termolecular recombination reactions.
- The chemical kinetics can be simplified by eliminating the need to write rate equations for the radical species involved, treating the fast reactions as if they were equilibrated.
- This treatment is call **the partial-equilibrium approximation**.

Partial equilibrium

For a hypothetic mechanism

$A+B_2 \rightarrow AB+B$	P.1f
$AB+B \rightarrow A+B_2$	P.1r
$B+A_2 \rightarrow AB+A$	P.2f
$AB+A \rightarrow B+A_2$	P.2r
$AB+A_2 \rightarrow A_2B+A$	P.3f
$A_2B+A \rightarrow AB+A_2$	P.3r
$A+AB+M \rightarrow A_2B+M$	P.4f

In this mechanism, the reactive intermediates are A, B and AB. The stable species are A_2,B_2 and A_2B.

Note that the bimolecular reactions are grouped as forward and reverser reaction pairs. The reactions of these pairs are much faster than the rate of the recombination reactions of P.4f.

Partial equilibrium

Bimolecular pairs behaving in this manner are often referred as **shuffle** reactions, since the radical species shuffle between being reactants and products.

We further assume that the forward and reverse reaction rates in each pair are equal, as

$$k_{P.1f}[A][B_2] = k_{P.1r}[AB][B]$$
$$k_{P.2f}[B][A_2] = k_{P.2r}[AB][A]$$
$$k_{P.3f}[AB][A_2] = k_{P.3r}[A_2B][A]$$

Or alternatively

$$\frac{[AB][B]}{[A][B_2]} = K_{p,1} = \frac{k_{p.1f}}{k_{p.1r}}$$
$$\frac{[AB][A]}{[B][A_2]} = K_{p,2}$$
$$\frac{[A_2B][A]}{[AB][A_2]} = K_{p,3}$$

Simultaneous solution of the above 3 equations allows the radical species A, B and AB to the expressed in terms of the stable species A_2,B_2, and A_2B, eliminating the need for rate equations for the radicals.

Partial equilibrium

$$[\mathrm{A}] = K_{p,3}(K_{p,1}, K_{p,2}[\mathrm{B}_2])^{1/2}\frac{[\mathrm{A}_2]^{3/2}}{[\mathrm{A}_2\mathrm{B}]},$$

$$[\mathrm{B}] = K_{p,3}K_{p,1}\frac{[\mathrm{A}_2][\mathrm{B}_2]}{[\mathrm{A}_2\mathrm{B}]},$$

$$[\mathrm{AB}] = (K_{p,1}, K_{p,2}[\mathrm{A}_2][\mathrm{B}_2])^{1/2}$$

Knowing the radical concentration from the above equations allows the product formation rate to be calculated from reaction P.4f.

$$\frac{\mathrm{d}[\mathrm{A}_2\mathrm{B}]}{\mathrm{d}t} = k_{P.4f}[\mathrm{A}][\mathrm{AB}][\mathrm{M}].$$

To evaluate and integrate this equation, $[A_2]$ and $[B_2]$ must be known or calculated from simultaneous integration of similar expressions.

Partial equilibrium

Discussion with regards to steady-state approximation

For both methods: a radical concentration is determined by an algebraic equation rather than the integration of an ordinary differential equation.

Difference:

Partial equilibrium approximation forces a reaction or sets of reactions, to be essentially equilibrated.

Steady-state approximation forces the individual net production rate of one or more species to be essentially zero.

Examples of using partial equilibrium approximation

- The calculation of carbon monoxide concentration during the expansion stroke of an SI engine
- The calculation of nitric oxide emission in turbulent jet flames

In both problems, the slow recombination reactions cause radical concentrations to build up to levels that are in excess of their values for full equilibrium.

Summary

- Global reaction and elementary reaction
- Bimolecular, termolecular and unimolecular reactions
- Molecular collision theory and reaction rates
- Steric factor, pre-exponential factor and activation energy
- Net species production rate, complex mechanism
- Chain reaction mechanism: chain initiation, chain propagation and chain termination
- The approximation of a steady state for highly reactive species to simplify chain mechanisms
- Partial equilibrium approximation
- Zeldovich nitric oxide formation mechanism
- Chemical time scales τ_{chem}