

Review on Chemical Kinetics

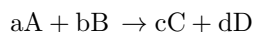
In this section, we will review some basic concepts on chemical kinetics and will try to connect them to the numerical methods we've studied so far. Chemical kinetics, also known as reaction kinetics, is a branch of physical chemistry focused on the study of rates and reaction mechanisms of chemical reactions. In chemical kinetics, reactions are not in equilibrium processes rather a time dependent one as many reactions could be considered "spontaneous", under the second law of thermodynamics, but the time for the to proceed could be long that in practice they never happen.

- For more details about chemical kinetics, **Chapter 17** of Physical Chemistry, Ira N. Levine is a good source.

We will begin by introducing some concepts,

- **Homogeneous reactions:** occur entirely in one phase, for example, gas-phase reactions and reactions in liquid solutions.
- **Heterogeneous reactions:** involves species present in two or more phases.

Rate of Reaction: In chemical kinetics, one of the key concepts is rate of reaction, commonly defined by r . Let's consider the following chemical reactions,



If we consider that this reaction happens in a closed system, the rate at which any of the reactants will be consumed should be proportional to the stoichiometric coefficient,

$$\frac{\frac{dn_A}{dt}}{\frac{dn_B}{dt}} = \frac{a}{b} \quad \text{and} \quad \underbrace{\frac{1}{a} \frac{dn_A}{dt}}_{f(A)} = \underbrace{\frac{1}{b} \frac{dn_B}{dt}}_{f(B)}$$

where n_A and n_B are the number of moles for the A and B species. This final relation is interesting as the left hand side only depends on the species A and the right hand side on the species B, mathematically this can only happen if both sides are equal to a constant, also known as **rate of conversion**, defined as

$$J = -\underbrace{\frac{1}{a} \frac{dn_A}{dt}}_{f(A)} = -\underbrace{\frac{1}{b} \frac{dn_B}{dt}}_{f(B)} = \underbrace{\frac{1}{c} \frac{dn_C}{dt}}_{f(C)} = \underbrace{\frac{1}{d} \frac{dn_D}{dt}}_{f(D)} \quad (1)$$

For any one-step chemical reaction, the rate of conversion has the following general notation,

$$J = \begin{cases} -\frac{1}{x} \frac{dn_X}{dt} & \text{if the species X is a reactant} \\ +\frac{1}{x} \frac{dn_X}{dt} & \text{if the species X is a product} \end{cases} \quad (2)$$

The rate of conversion is an extensive quantity as it depends on the number of moles, we can make it an intensive quantity by considering the conversion rate by volume, J/V . If the chemical reaction happens in a constant volume, we can express the rate of conversion in terms of molar concentration,

$$r = \frac{J}{V} = \begin{cases} -\frac{1}{x} \frac{d[X]}{dt} & \text{if the species X is a reactant} \\ +\frac{1}{x} \frac{d[X]}{dt} & \text{if the species X is a product} \end{cases} \quad (3)$$

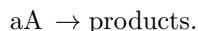
Rate Laws: For a chemical reaction, the rate r at time t can be determined experimentally and be related to the concentrations of species at time t using the following general form,

$$r = k[A]^\alpha[B]^\beta \dots \quad (4)$$

the exponents α , and β **are not** the stoichiometric coefficients, they are called the **partial order** coefficients, as they determine the dependence of the reaction rate with respect to each species. The sum of the partial order coefficients tells us the **overall order** of the reaction. k is the **rate constant**, and it depends on the pressure and temperature at which the chemical reaction is happening. In this notes, we will see that the rate law is determined from experimental measurements as it cannot be deduced from the reaction stoichiometry.

1 Integration of Rate Laws

Kinetics experiments are designed to measure the concentration of the species involved in a chemical reaction over the time it happens. These processes can be modelled/described using differential equations, $\frac{dx}{dt} = f(x(t))$, where x will be the concentration of a species at time t . For all the following types of reactions, let's consider the following chemical reaction,



1.1 First-Order Reactions

The rate law and rate of conversion of this chemical reaction are,

$$r = k[A]^\alpha \quad \text{and} \quad r = -\frac{1}{a} \frac{d[A]}{dt}, \quad (5)$$

if we equate both of them and define $k_a = ak$, and $\alpha = 1$ we get the following differential equation,

$$\frac{d[A]}{dt} = -k_a[A] \quad (6)$$

we can solve this differential equation by using the following trick,

$$\frac{d[A]}{[A]} = -k_a dt, \quad (7)$$

where the left hand-side only depends on $[A]$, and the right-hand side on time. We can integrate this equation,

$$\int_{[A]_{t_0}}^{[A]_{t_1}} \frac{d[A]}{[A]} = \int_{t_0}^{t_1} -k_a dt, \quad (8)$$

giving us,

$$[A]_{t_1} = [A]_{t_0} e^{-k_a(t_1-t_0)}. \quad (9)$$

This equation tells us that the time factor $e^{-k_a(t_1-t_0)}$ is an exponential decay. For first-order reactions we can define the *half-life* time, $t_{1/2}$, as the time it takes to consume half of the original concentration of A,

$$\frac{[A]_{t_1}}{[A]_{t_0}} = \frac{1}{2} = e^{-k_a(t_1-t_0)} \rightarrow k_a t_{1/2} = \ln 2 \approx 0.693, \quad (10)$$

indicating us that for first-order reaction the half-life time is independent of the initial concentration.

1.2 Second-Order Reactions

For second-order reactions, the rate law and rate of conversion of this chemical reaction are,

$$r = k[A]^2 \quad \rightarrow \quad \frac{d[A]}{dt} = -k_a[A]^2 \quad (11)$$

where $\alpha = 2$. Using the similar trick to solve this differential equation, we get,

$$\frac{1}{[A]_{t_1}} = \frac{1}{[A]_{t_0}} + k_a(t_1 - t_0). \quad (12)$$

The half-life time for second order reactions is,

$$t_{1/2} = \frac{1}{[A]_{t_0} k_a}. \quad (13)$$

Contrary to first-order reaction, the half-life time of second-order reactions does depend on the initial concentration of the reactant.

1.3 nthOrder Reactions

We can extend the same procedure to reactions of nth-order, $\alpha = n$, where the rate law and rate of conversion of this chemical reaction are,

$$r = k[A]^n \quad \rightarrow \quad \frac{d[A]}{dt} = -k_a[A]^n. \quad (14)$$

This differential equation has a general solutions for any $n \neq 1$,

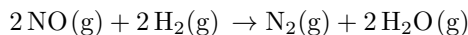
$$\left(\frac{[A]_{t_1}}{[A]_{t_0}} \right)^{1-n} = 1 + [A]_{t_0}^{n-1} (n-1) k_a (t_1 - t_0). \quad (15)$$

The half-life time for these general reactions is,

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)[A]_{t_0}^{n-1} k_a}. \quad (16)$$

2 Determining the Rate Law from Experiments

The “fitting” of rate laws using experimental data can be done using all the toolkit from non-linear and liner equations that we have studied. For that we will consider the following example,



The following data was collected at $T = 1280^\circ\text{C}$,

Experiment	[NO]	[H ₂]	Initial rate
1	0.005	0.002	1.25×10^{-5}
2	0.01	0.002	5×10^{-5}
3	0.01	0.004	10^{-4}

We can use this data to find the values of rate constant (k) and the partial order coefficients of the following rate law,

$$r = k[\text{NO}]^\alpha [\text{H}_2]^\beta \quad (17)$$

We can transform this equation into a linear one using \ln ,

$$\ln r = \ln k + \alpha \ln[\text{NO}] + \beta \ln[\text{H}_2] = \underbrace{[\ln k, \alpha, \beta]}_{\text{parameters}} \underbrace{\begin{bmatrix} 1 \\ \ln[\text{NO}] \\ \ln[\text{H}_2] \end{bmatrix}}_{\mathbf{x}} \quad (18)$$

Using this representation we get three linear equations, one for each experiment. The linear set of equations that we must solve are,

$$\underbrace{\begin{bmatrix} 1 & \ln 0.005 & \ln 0.002 \\ 1 & \ln 0.01 & \ln 0.002 \\ 1 & \ln 0.01 & \ln 0.004 \end{bmatrix}}_{\mathbf{A}} \underbrace{\begin{bmatrix} \ln k \\ \alpha \\ \beta \end{bmatrix}}_{\mathbf{x}} = \underbrace{\begin{bmatrix} \ln 1.25 \times 10^{-5} \\ \ln 5 \times 10^{-5} \\ \ln 10^{-4} \end{bmatrix}}_{\mathbf{b}} \quad (19)$$

We can solve this $\mathbf{A} \mathbf{x} = \mathbf{b}$ linear set of equation using Gauss-Jordan elimination, but this time I will introduce another method to find \mathbf{x} .

2.1 Inverse of a Matrix Method

Given a system of linear equations $\mathbf{A} \mathbf{x} = \mathbf{b}$, \mathbf{x} can be found using the inverse if \mathbf{A}^{-1} . This method only work if \mathbf{A} is a square matrix, meaning same number of rows and columns.

$$\begin{aligned} \mathbf{A} \mathbf{x} &= \mathbf{b} \\ \mathbf{A}^{-1} \mathbf{A} \mathbf{x} &= \mathbf{A}^{-1} \mathbf{b} \quad \text{remember that} \quad \mathbf{A}^{-1} \mathbf{A} = \mathbf{I} \\ \mathbf{x} &= \mathbf{A}^{-1} \mathbf{b} \quad \text{where} \quad \mathbf{I} \mathbf{x} = \mathbf{x} \end{aligned} \quad (20)$$

If we can invert \mathbf{A} then, we can find the value of \mathbf{x} for this linear equations. The following Python code shows us how we can solve this problem using Numpy.

```

1  import numpy as np
2
3  X = np.array([[0.0050,0.002],
4               [0.01,0.002],
5               [0.01,0.004]])
6  X = np.log(X)
7  X = np.column_stack((np.ones(3,), X))
8
9  y = np.array([1.25E-5,5E-5, 1E-4])
10 y = np.log(y)
11
12 # solve the linear equations with Numpy
13 w = np.linalg.solve(X,y)
14
15 ln_k = w[0]
16 alpha = w[1]
17 beta = w[2]
```

Listing 1: Python Code