

# Modeling Chemical Reactions

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## 1 Modeling Reactors

The most basic chemical reactor model is a continuously stirred tank reactor (CSTR) as illustrated in Figure 1a. Networks of CSTRs can be used to approximate essentially any other reactor (within reason) arbitrarily well; see for example Figures 1b & 1c. In combination with their simplicity, they lay the foundation for the computational treatment of more complicated settings where chemical reactions play an important role, for example reactive fluids.

Further assuming that pressure and temperature are externally imposed, then the reactor is thermodynamically fully characterized in terms of mole balances for all chemical species/constituents:

$$\frac{dn_i}{dt} = \dot{n}_{i,in} - \dot{n}_{i,out} + V \sum_{k=1}^{N_R} \hat{r}_{i,k}(\mathbf{c}, p, T)$$

where

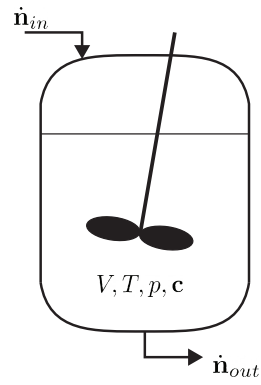
- $n_i$  refers to the number of moles of species/constituent  $i$
- $\dot{n}_{i,in}$  ( $\dot{n}_{i,out}$ ) refers to the mole flow rate into (out of) the reactor
- $V$  refers to the volume of the *fluid* in the reactor
- $\hat{r}_{i,k}$  refers to the rate of formation/consumption of species  $i$  due to reaction  $k$
- $\mathbf{c} = [c_1, \dots, c_N]$  refers to the composition of the fluid (usually in molar concentration of all the constituents but sometimes different abstractions (mole fractions, mass fractions, chemical potential, ...) are more appropriate.)
- $T$  refers to the temperature in the fluid
- $p$  refers to the pressure in the fluid

In practice, often further simplifications apply. For example, in many situations it is warranted to assume that the fluid volume is constant and independent of composition. Under this assumption, the model reduces to the commonly used form

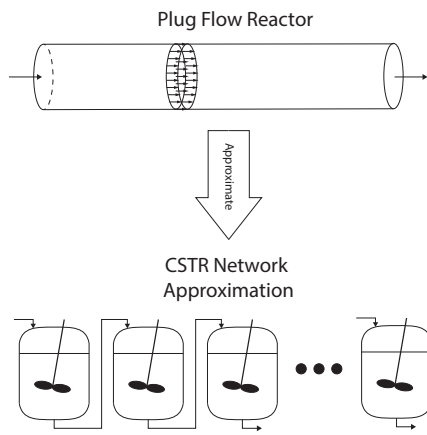
$$\frac{dc_i}{dt} = D(c_{i,in} - c_i) + \sum_{k=1}^{N_R} \hat{r}_{i,k}(\mathbf{c}, p, T)$$

where

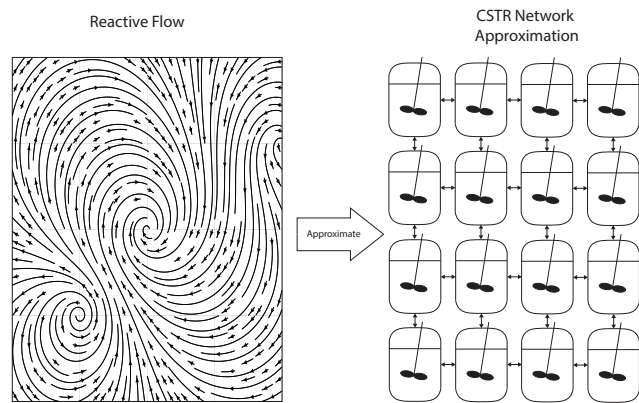
- $c_i = \frac{n_i}{V}$  refers to the molar concentration of species/constituent  $i$



(a) CSTR schematic



(b) Approximation of plug flow reactor.



(c) Approximation of reactive flow.

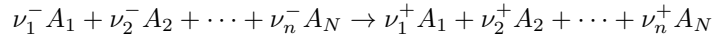
Figure 1: CSTR as key building block for modeling chemical reactions.

- $D = \frac{\dot{V}}{V}$  refers to the throughput rate (note that  $\dot{V} = \dot{V}_{in} = \dot{V}_{out}$  by assumption)
- $\mathbf{c} = [c_1, \dots, c_N]$  refers to the composition of the fluid (usually in molar concentration of all the constituents but sometimes different abstractions (mole fractions, mass fractions, chemical potential, ...) are more appropriate.)
- $T$  refers to the temperature in the fluid
- $p$  refers to the pressure in the fluid

In the following sections, we discuss how the reaction terms  $\hat{r}_{i,k}$  are treated computationally, introduce simple models and discuss stiffness.

## 2 Modeling Chemical Reactions

On a fundamental level, chemical reactions are described as discrete transitions of the form



which is to be parsed as:  $\nu_1^-$  molecules of species  $A_1$ ,  $\nu_2^-$  molecules of species  $A_2$ , ..., and  $\nu_n^-$  molecules of species  $A_N$  react to form  $\nu_i^+$  molecules of species  $A_i$ .

This microscopic model translates 1-1 into the macroscopic description where the formation/consumption rate of species  $A_i$  due to reaction  $k$  is given by

$$\hat{r}_{i,k}(\mathbf{c}, T, p) = (\nu_{i,k}^+ - \nu_{i,k}^-) \hat{r}_k(\mathbf{c}, T, p)$$

where  $r_k$  is the rate of reaction  $k$ .

This leads to a rather dense and convenient description of CSTR models

$$\frac{d\mathbf{n}}{dt} = \dot{\mathbf{n}}_{in} - \dot{\mathbf{n}}_{out} + V \mathbf{S} \mathbf{r}(\mathbf{c}, T, p)$$

where

- $\mathbf{n} = [n_1, \dots, n_N]$  refers to the mole counts of the chemical species
- $\dot{\mathbf{n}}_{in} = [\dot{n}_{1,in}, \dots, \dot{n}_{N,in}]$  ( $\dot{\mathbf{n}}_{out}$ ) refers to the molar inlet (outlet) flowrate of the chemical species
- $V$  refers to the fluid volume
- $\mathbf{S}$  refers to the *stoichiometry matrix* with  $\mathbf{S}_{i,k} = \nu_{i,k}^+ - \nu_{i,k}^-$
- $\mathbf{r}(\mathbf{c}, T, p) = [r_1(\mathbf{c}, T, p), \dots, r_{N_R}(\mathbf{c}, T, p)]$  refers to the reaction rates
- $T$  refers to the temperature in the fluid
- $p$  refers to the pressure in the fluid.

The last puzzle piece required to complete the reactor model is a constitutive relation that maps the composition, temperature and pressure to the reaction rates  $r_k$ . For such models, one can draw from the rich and deep theory of chemical kinetics an overview of which is beyond the scope of this introduction. Due to their practical relevance we will restrict our review here to mass-action based kinetics:

$$r_k(T, p) = k(T) \prod_{i=1}^N c_i^{|\nu_{i,k}^-|}.$$

This relation structure can be justified by statistical mechanics considerations which give further insights with regard to the validity of this model. The temperature-dependence of the reaction rate "constant"  $k(T)$  itself can be modeled in various ways. A very popular functional form that is found to be phenomenologically correct in many settings and can be justified via transition state theory is the modified Arrhenius equation:

$$k(T) = AT^n e^{-\frac{E_a}{k_B T}}$$

where

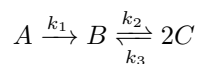
- $A$  is an *actual* constant
- $E_a$  the activation energy barrier
- $k_B$  the Boltzmann constant
- $T$  temperature.

The parameters of this relation are the constant  $A$ , exponent  $n$ , and activation energy  $E_a$ . These can be found in the literature for a wide range of reactions, or alternatively be computed ab initio with quantum chemical models.

### 3 Chemical Reactions and Stiffness

The computational study of chemical reactions highlights a fundamental challenge for the numerical solution of ODEs: stiffness. In the context of dynamical systems, stiffness refers loosely speaking to the separation of time scales into \*fast\* and \*slow\* components. This causes problems for numerical integration as one is required to resolve the fast dynamics, which intuitively speaking means one is restricted to small time steps, while also requiring long simulation horizons to observe the slow dynamics take effect; overall, a large number of time steps is needed for an accurate solution, rendering the simulation expensive.

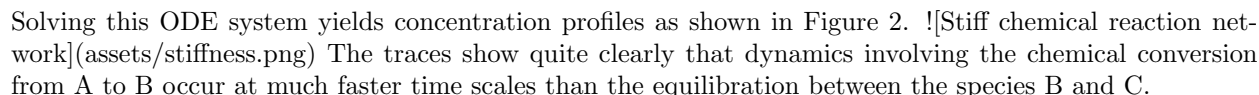
Chemical reactions are notorious for giving rise to stiff dynamical systems (the time scales at which the reactions in a single reactor take place can vary across many orders of magnitude). A simple example for that is given by the generic reaction network



Assuming isochoric and isothermal operation, a CSTR (without in and outlet streams) can be modeled as

$$\frac{d}{dt} \begin{bmatrix} c_A \\ c_B \\ c_C \end{bmatrix} = \underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 1 & -1 & 1 \\ 0 & 2 & -2 \end{bmatrix}}_{=\mathbf{S}} \underbrace{\begin{bmatrix} k_1 c_A \\ k_2 c_B \\ k_3 c_C^2 \end{bmatrix}}_{=\mathbf{r}(c,T,p)}$$

with reaction rate constants  $k = [100 \frac{1}{s}, 0.25 \frac{1}{s}, 1 \frac{L}{mol \cdot s}]$ .

Solving this ODE system yields concentration profiles as shown in Figure 2.  The traces show quite clearly that dynamics involving the chemical conversion from A to B occur at much faster time scales than the equilibration between the species B and C.

### 4 Stability in the presence of stiffness

Against the backdrop of the considerations of the previous section, one may be tempted to suspect that unless we care about accurate predictions at early times, stiffness may not result in increased simulation

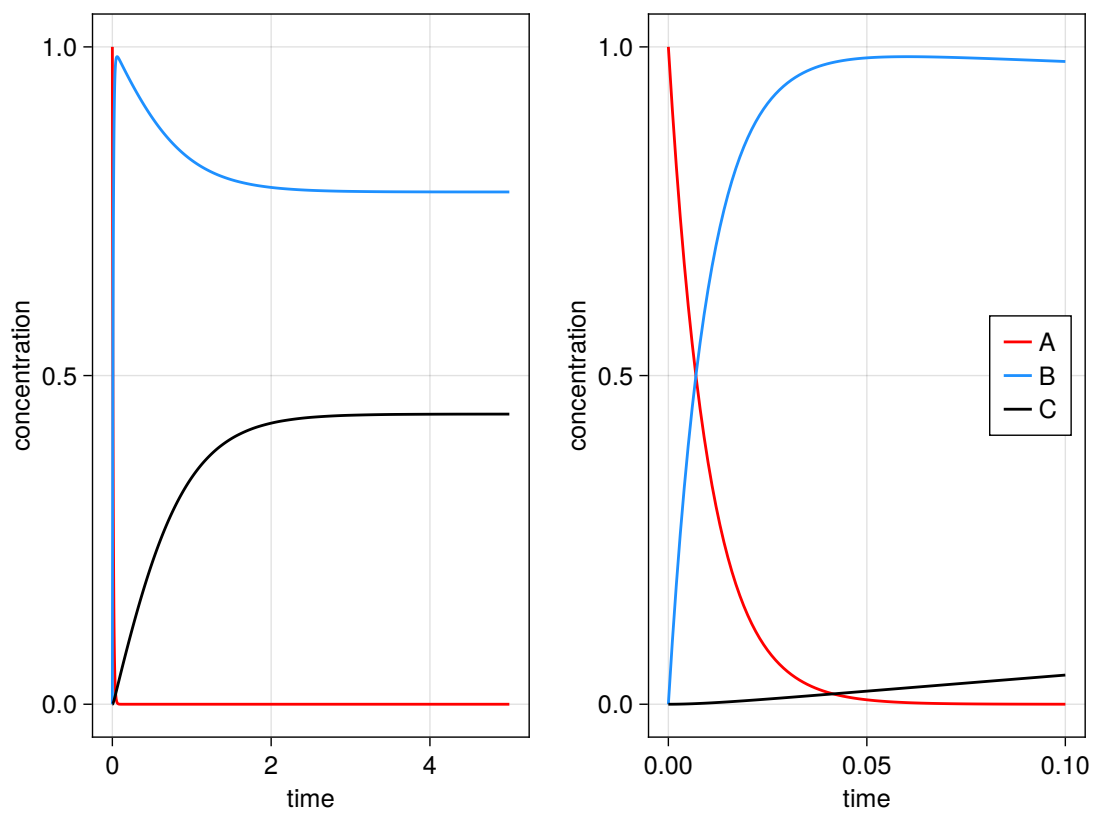


Figure 2: Concentration profiles of stiff reaction system.

cost; after all if we do not care about the prediction at early times, we may be tempted to simply use large time steps in the integration to resolve only the slow dynamics. This suspicion of course is misguided as dynamical systems described by ODEs are inherently causal so that changes at early times may profoundly affect the behavior at later times. In practice, we this issue often manifests as instability of the numerical integration routine. In the following, we briefly discuss the basics of analyzing the stability of numerical integration routines and discuss how this pertains to stiffness.

The simplest framework in which the stability properties of numerical integrators are commonly studied is Dahlquist's test equation:

$$\frac{dx}{dt} = \lambda x$$

Specifically, the region of stability of a given numerical integrator  $\phi$  is the set  $\{\lambda h \in \mathbb{C} : \lim_{k \rightarrow \infty} |x(kh)| = 0\}$ , i.e., the region where the recursion

$$x((k+1)h) = \phi(x(kh), y \mapsto \lambda y, h)$$

is asymptotically stable.

The region of stability of the analytical integrator is of course the left half-plane, i.e.,  $\{\lambda h \in \mathbb{C} : \text{Re}(\lambda h) < 0\}$ . However, for instance the region of stability for the explicit Euler method is only a small subset of that; specifically, it is merely the unit disk in the imaginary plane centered at  $(-1,0)$ :  $\{\lambda h \in \mathbb{C} : |\lambda h + 1| \leq 1\}$ .<sup>1</sup> Put differently, the explicit Euler method may predict instable trajectories when the true solution is actually stable - clearly undesirable. In contrast, the region of stability for the implicit Euler method is  $\{\lambda h \in \mathbb{C} : |1 - \lambda h| \geq 1\}$ , i.e., the complement of the unit disk in the imaginary plane centered at  $(1,0)$ .<sup>2</sup> Or put differently again, the implicit Euler method may predict stable trajectories when the true solution does not - also clearly undesirable. We see that, at least for these two integrators, the stability properties depend fundamentally on the ratio of the time scale of the dynamics  $\frac{1}{|\lambda|}$  and the integration step size  $h$ . Broadly speaking, fast time scales necessitate small time steps to ensure stable integration. As stiff systems are characterized by the presence of fast and slow time-scales, we are therefore trapped in the dilemma of requiring many small integration steps.

## 5 Implicit Time-Stepping

## 6 Runge-Kutta Methods

## 7 Adaptive Time-Stepping

## 8 Exercises

### 8.1 Various time-stepping methods

In this exercise we wish to compare to the stability and performance properties of different integration schemes. To that end, complete the code template that implements the following four integration routines

- Explicit Euler
- Implicit Euler

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<sup>1</sup>Exercise: verify this yourself

<sup>2</sup>Exercise: verify this yourself

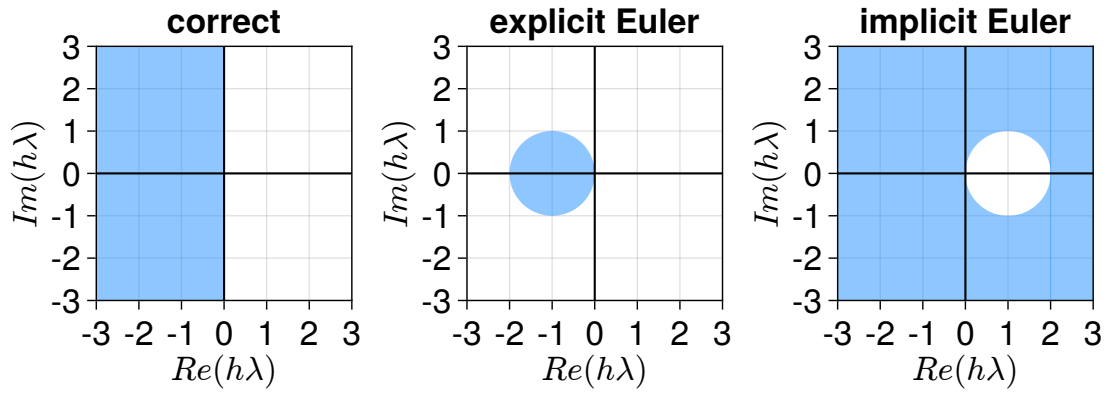
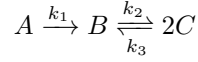


Figure 3: Region of stability for implicit, explicit & analytical integrators.

- Crank-Nicolson's method
- Heun's method

and apply it to the simulation of an isothermal, isochoric CSTR without inlet and outlet streams. The underlying reaction network is given by



with reaction rate constants  $k = [100\frac{1}{s}, 0.25\frac{1}{s}, 1\frac{L}{mol \cdot s}]$  and initial concentration  $\mathbf{c}_0 = [1, 0, 0]$  over a horizon of  $t \in [0, 10.0]$ . The kinetics follow mass action kinetics.

Specifically, simulate this system with all different methods for the step sizes  $h \in \{10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, 1, 10\}$  and compare

- the trajectories of the concentrations  $c_A(t), c_B(t), c_C(t)$  predicted by each method by plotting the traces for each step size  $h$ .
- the computational efficiency of each method by plotting the time required for integration as a function of the step size  $h$
- the accuracy of each method by comparing the computed result  $c_A(0.01)$  to the analytical solution  $c_{A,\text{exact}}(0.01) = c_{A,0}/e$  for each step size  $h$ .

Table 1: Integrators

Method	Time-stepping rule
Explicit Euler	$x_{k+1} = x_k + hf(x_k, t_k)$
Implicit Euler	$x_{k+1} = x_k + hf(x_{k+1}, t_k + h)$
Heun's Method	$y = x_k + hf(x_k, t_k)$ $x_{k+1} = x_k + \frac{h}{2} (f(x_k, t_k) + f(y, t_k + h))$
Crank-Nicolson Method	$x_{k+1} = x_k + \frac{h}{2} (f(x_k, t_k) + f(x_{k+1}, t_k + h))$

## 8.2 Ionospheric chemistry model

Schunk [1988] proposes the reaction network with associated phenomenological rate coefficients as shown in Figures 4 & 5 to capture the dominant chemical phenomena in the ionosphere.

Is the associated reaction system is stiff? Why or why not?

Complete the template ionosphere chemistry model and set up a simulation that describes the trajectory of



Reaction	Rate Coefficients, $\text{cm}^3 \text{s}^{-1}$	Source
$\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{O}$	$k_1$	(a)
$\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}$	$k_2$	(a)
$\text{O}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}$	$k_3$	(a)
$\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$	$5 \times 10^{-16}$	(b)
$\text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2$	$4.4 \times 10^{-10}$	(c)
$\text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}$	$1.2 \times 10^{-10}$	(d)
$\text{O}_2^+ + e \rightarrow \text{O} + \text{O}$	$1.6 \times 10^{-7} (300/T_e)^{0.55}$	(e)
$\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$	$1.4 \times 10^{-10} (300/T)^{0.44}; T \leq 1500^\circ \text{K}$ $5.2 \times 10^{-11} (T/300)^{0.2}; T > 1500^\circ \text{K}$	(f)
$\text{N}_2^+ + \text{O} \rightarrow \text{O}^+ + \text{N}_2$	$1 \times 10^{-11} (300/T)^{0.23}; T \leq 1500^\circ \text{K}$ $3.6 \times 10^{-12} (T/300)^{0.41}; T > 1500^\circ \text{K}$	(f)
$\text{N}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}_2$	$5 \times 10^{-11} (300/T)$	(g)
$\text{N}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}_2$	$3.3 \times 10^{-10}$	(h)
$\text{N}_2^+ + e \rightarrow \text{N} + \text{N}$	$1.8 \times 10^{-7} (300/T_e)^{0.39}$	(i)
$\text{NO}^+ + e \rightarrow \text{N} + \text{O}$	$4.2 \times 10^{-7} (300/T_e)^{0.85}$	(j)
$\text{He}^+ + \text{N}_2 \rightarrow \text{N}^+ + \text{N} + \text{He}$	$1 \times 10^{-9}$	(c)
$\text{N}^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{O}$	$2 \times 10^{-10}$	(c)
$\text{N}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}$	$4 \times 10^{-10}$	(c)
$\text{N}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}$	$2 \times 10^{-11}$	(k)

- (a) ALBRITTON *et al.* [1977]; ST.-MAURICE and TORR [1978].  
(b) FITE [1969].  
(c) LINDINGER *et al.* [1974]; HUNTRESS and ANICICH [1976].  
(d) FEHSENFELD [1977].  
(e) MEHR and BIONDI [1969]; WALLS and DUNN [1974]; TORR *et al.* [1976b].  
(f) MCFARLAND *et al.* [1974]; TORR *et al.* [1977].  
(g) MCFARLAND *et al.* [1973]; LINDINGER *et al.* [1974].  
(h) FEHSENFELD *et al.* [1970].  
(i) MEHR and BIONDI [1969].  
(j) WALLS and DUNN [1974]; TORR *et al.* [1976a].  
(k) KOSMIDER and HASTED [1975].

Figure 4: Ionospheric Reaction Network

$$k_1 = 1.533 \times 10^{-12} - 5.92 \times 10^{-13}(T/300) + 8.60 \times 10^{-14}(T/300)^2; \\ 300 \leq T \leq 1700^\circ\text{K} \quad (54a)$$

$$k_1 = 2.73 \times 10^{-12} - 1.155 \times 10^{-12}(T/300) + 1.483 \times 10^{-13}(T/300)^2; \\ 1700 < T < 6000^\circ\text{K} \quad (54b)$$

$$k_2 = 2.82 \times 10^{-11} - 7.74 \times 10^{-12}(T/300) + 1.073 \times 10^{-12}(T/300)^2 \\ - 5.17 \times 10^{-14}(T/300)^3 + 9.65 \times 10^{-16}(T/300)^4; \\ 300 \leq T \leq 6000^\circ\text{K} \quad (55)$$

$$k_3 = 8.36 \times 10^{-13} - 2.02 \times 10^{-13}(T/300) + 6.95 \times 10^{-14}(T/300)^2; \\ 320 < T < 1500^\circ\text{K} \quad (56a)$$

$$k_3 = 5.33 \times 10^{-13} - 1.64 \times 10^{-14}(T/300) + 4.72 \times 10^{-14}(T/300)^2 \\ - 7.05 \times 10^{-16}(T/300)^3; \quad 1500 < T < 6000^\circ\text{K} \quad (56b)$$

Figure 5: Reaction rate constants

the composition in a *closed* CSTR from the following initial composition:

$$\begin{aligned} c_{0,e} &= 6 \times 10^8 \frac{1}{\text{cm}^3} \\ c_{0,O} &= 0 \frac{1}{\text{cm}^3} \\ c_{0,O^+} &= 10^8 \frac{1}{\text{cm}^3} \\ c_{0,O_2} &= 2.1 \times 10^8 \frac{1}{\text{cm}^3} \\ c_{0,O_2^+} &= 10^8 \frac{1}{\text{cm}^3} \\ c_{0,N} &= 0 \frac{1}{\text{cm}^3} \\ c_{0,N^+} &= 10^8 \frac{1}{\text{cm}^3} \\ c_{0,N_2} &= 7.9 \times 10^7 \frac{1}{\text{cm}^3} \\ c_{0,N_2^+} &= 10^8 \frac{1}{\text{cm}^3} \\ c_{0,NO} &= 0 \frac{1}{\text{cm}^3} \\ c_{0,NO^+} &= 10^8 \frac{1}{\text{cm}^3} \\ c_{0,He} &= 0 \frac{1}{\text{cm}^3} \\ c_{0,He^+} &= 10^8 \frac{1}{\text{cm}^3} \end{aligned}$$

Assume the temperature is constant at  $T = 2000$  K.

You can use the implemented integrators from the previous problem or any available ODE solver library.

### 8.3 Reaction-Diffusion-Advection Equation

Make a Poisson equation example in the next session, perhaps diffusing dimerization example?

### References

RW Schunk. A mathematical model of the middle and high latitude ionosphere. *Pure and applied geophysics*, 127(2):255–303, 1988.