202. Chemical reactions are dynamical

What new skills will I possess after completing this laboratory?

- **Applying** DynamicalSystems and GLMakie to set up a dynamical system.
- **Developing** a dynamical system from chemical equations.

Why do I need these skills?

A ***dynamical system*** is a set of ***state*** (or ***phase***) ***variables*** $\boldsymbol{x} \equiv (x_1, x_2, \dots)$ whose rates of change are described by a set of ***ordinary differential equations*** (ODEs) $\dot{\boldsymbol{x}} = \boldsymbol{f}(\boldsymbol{x}, t)$. If $\boldsymbol{f}$ depends upon t, we say that the system is ***driven***; otherwise it is ***autonomous***.

Dynamical systems arise in all areas of the sciences – we will start by looking at their application to chemical reactions.

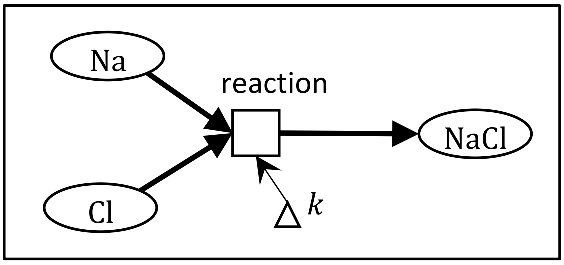
The chemical law of mass action: The rate of change of the concentrations of the various chemical species in an ***elementary*** (or one-step) chemical reaction is proportional to the concentrations of these species.

Proof: If a chemical reaction involves molecules A and B coming together within a small volume *V*, the probability that the reaction will occur is equal to the probability that *both A and B* are within *V*. But in a one-step reaction this is just the product of the probabilities that each of A or B is present within *V*, which are proportional to the concentrations of A and B.

Example: Give an expression for the rate of the chemical reaction of sodium Na and chlorine Cl to form salt NaCl, and build a model to simulate this reaction.

Solution: The reaction is $\mathrm{Na} + \mathrm{Cl} \rightarrow \mathrm{NaCl}$. Denoting the species concentrations $n \equiv [\mathrm{Na}]$, $c \equiv [\mathrm{Cl}]$ and $s \equiv [\mathrm{NaCl}]$, and using the law of mass action, the reaction rate is $r \equiv \dot{s} = k\,n\,c$, where k is the **rate constant** of this reaction.

To model this reaction, first create its SPD as shown on the right.



Now consider that NaCl increases at the reaction rate r, while Na and Cl *decrease* at the rate r. This gives you the differential equations for the entire chemical reaction.

(i) Now use the template file **ReactionKinetics.jl** to set up and run the dynamical model of the above example, using the simple values $k = 1$, $[\mathrm{Na}]_0 = 1.0$ and $[\mathrm{Cl}]_0 = 1.0$. Explain the plot you obtain.

(ii) Slightly confusingly, your plot currently places the two reactant curves on top of each other. Check the individual trajectories by switching off first one and then the other reactant curve.

What is the structure of the skills?

The law of mass action is a simple idea that describes a wide variety of chemical transformations. The instantaneous rate of a chemical reaction $\alpha X_\alpha + \beta X_\beta + \cdots \rightarrow \rho Y_\rho + \sigma Y_\sigma + \cdots$ is defined by the reaction's chemical concentrations and its reaction constant k according to the following **rate law**:

$$(1) \quad r \equiv k\,[X_\alpha]^a\,[X_\beta]^b \cdots [Y_\rho]^r\,[Y_\sigma]^s \cdots$$

This leads to the following rates of change of the reactants and products:

(2) $r = -\frac{1}{\alpha}\frac{d[X_\alpha]}{dt} = -\frac{1}{\beta}\frac{d[X_\beta]}{dt} = \cdots = \frac{1}{\rho}\frac{d[X_\rho]}{dt} = \frac{1}{\sigma}\frac{d[X_\sigma]}{dt} = \cdots$

For one-step reactions the reactant exponents $a, b, \ldots$ are equal to the reactant coefficients $\alpha, \beta, \ldots$, and the product exponents $m, n, \ldots$ are zero. However many important reactions are non-elementary, involving back-reactions from the products, enzymatic influences and possible inhibitors. In such cases we must use experiments to determine the relation between exponents and coefficients.

(iii) Adapt the **ReactionKinetics** module to create a new model for the reaction of sulphate and hydrogen ions into bisulphate ions: $\mathrm{SO}_3^{2-} + H^+ \leftrightarrow \mathrm{HSO}_3^-$. This reaction is reversible, so we set up the differential equations for both directions. Let $s \equiv [\mathrm{SO}_3^{2-}]$, $h \equiv [H^+]$, $b \equiv [\mathrm{HSO}_3^-]$, then $\dot{s} = \dot{h} = -k_1 sh + k_{-1}b$, and $\dot{b} = k_1 sh - k_{-1}b$, where k_1, k_{-1} are respectively the forward and backward reaction constants. Run this model, then investigate the effect of varying the reaction constants.

How can I extend my skills?

(iv) Try plotting the salt-formation model in three dimensions, viewing the reactants and the product on two axes, with time on a third axis.

How can I deepen my practice of the skills?

(v) Set up and run a model of the combustion of hydrogen H and oxygen O to form water $\mathrm{H_2O}$ (rate constant 0.005). *Be careful:* This is a **second-order** reaction – there must be *one* oxygen and *two* hydrogen atoms present for the reaction to take place, so what will this mean for the exponent of H in the rate law (1)?