

Abstract

Chemical kinetics is the branch of chemistry that measures rates of chemical reactions, studies the factors that influence them, designs and prepares new catalysts, and interprets the results at the molecular level. The independent variable of chemical kinetics, from the chemical reaction starting moment when the reactants are mixed to its final moment when equilibrium is reached, is time, a variable introduced by the second law of thermodynamics for irreversible processes. The first study of the rate of a chemical reaction is credited to Ludwig Wilhelmy in 1850 for the decomposition of sucrose (table sugar) into glucose and fructose, in acid medium. Wilhelmy found that the rate of this chemical reaction is proportional to the existing amount of sucrose at each instant in the course of the chemical reaction. This chapter begins with sections on the rate of a chemical reaction, the experimental rate equation, and the effect of temperature change. We then consider elementary reactions, complex reactions, and extremely fast reactions. Most chemical reactions function like one-way streets: the concentrations of reactants decrease, those of reaction intermediates increase at first and decrease later, and the concentrations of products increase. However, for a few reactions far from equilibrium, the concentrations of some intermediate species oscillate, increasing and decreasing repeatedly. These reactions are illustrated with the Brusselator, a model chemical oscillator developed in the Brussels thermodynamic school founded by Prigogine. At the end of this chapter, the student can find two notes on matrix diagonalization and systems of first-order linear differential equations, useful for understanding the mathematical treatment given to the Brusselator, two Mathematica codes (First-Order Chemical Reaction, Brusselator) with references to expressions in the main text, detailed explanations for new commands and suggestions for the student to follow, a glossary that explains important scientific terms, and a list of exercises, whose complete answers can be found at the end of the book.

2.1 Rate of a Chemical Reaction

Add bleach (typically a solution of sodium hypochlorite) to a food dye in aqueous solution. This simple experiment can illustrate the change of concentration of the dye as a function of time. Let us call the dye A and assume that its initial concentration is $[A]_0 = 5.0 \times 10^{-5} \text{ M}$. The continuous addition of bleach causes progressive discoloring. The spectral absorbance of such a diluted solution is proportional to the concentration of the absorbing species (Beer–Lambert law). This empirical, relationship makes it possible to determine the dye concentration from absorbance measurements taken at an absorption maximum wavelength (λ_{max}). Since the initial concentration of the dye is very low, the bleach exists in large excess as compared with the dye. Hence, the bleach concentration does not appreciably change during dye discoloring and the chemical reaction can be represented in the following way

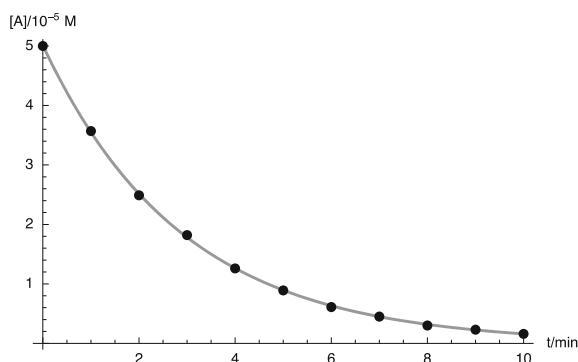


where B represents the colorless form of the dye (the bleach is omitted because its concentration is approximately constant during the experiment). The following table gives the concentration of A as a function of time at 1-min intervals.

t/min	0	1	2	3	4	5	6	7	8	9	10
$[A]/10^{-5} \text{ M}$	5.00	3.57	2.49	1.82	1.26	0.89	0.61	0.45	0.30	0.23	0.16

The graph of $[A]$ as a function of t is called a **kinetic reaction profile** for the chemical reaction (2.1) and is presented in Fig. 2.1 (see *Mathematica* code **M1**). Once the fitting curve is known (an exponential, as we will soon find out), it is possible to obtain the derivative at each instant in the considered time range. Since A is the reactant, $[A]$ is a decreasing function of time, its first derivative is negative, and the **reaction rate** is given by $-d[A]/dt$. The reaction rate defined using B is given by $d[B]/dt$, that is, $d[B]/dt = -d[A]/dt$ (**E1**).

Fig. 2.1 Typical kinetic reaction profile for discoloration of a dye. Figure obtained with *Mathematica*



Considering now the chemical reaction



[for example, $H_2(g) + I_2(g) \rightarrow 2HI(g)$], we can write

$$dn_C = 2(-dn_A) = 2(-dn_B) \quad (2.3)$$

where dn_A , dn_B , and dn_C represent changes in the molar quantities of A, B, and C. Both dn_A and dn_B are negative, because A and B are reactants, dn_C is positive (C is the single product) and is twice $-dn_A$ or $-dn_B$ [see (2.2)]. From (2.3), we can write

$$\frac{dn_A}{-1} = \frac{dn_B}{-1} = \frac{dn_C}{2} \quad (2.4)$$

where the denominators are the stoichiometric numbers (=stoichiometric coefficients, where the stoichiometric coefficients of reactants are multiplied by -1). For the generic chemical reaction



we can write

$$\frac{dn_A}{-a} = \frac{dn_B}{-b} = \frac{dn_C}{c} = \frac{dn_D}{d} \equiv d\xi \quad (2.6)$$

where ξ is called the **extent** of the chemical reaction that specifies the variable composition along the course of the chemical reaction (ξ is a state variable). If the chemical reaction (2.5) is carried out at constant volume, then

$$\frac{1}{-a} \frac{d[A]}{dt} = \frac{1}{-b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} = \frac{1}{V} \frac{d\xi}{dt} \quad (2.7)$$

where the square brackets stand for molarity. Each member of (2.7) defines the rate of the chemical reaction that can be obtained at any specified instant during the course of the chemical reaction (E2). Note that (2.7) assumes a time-independent stoichiometry, that is, the reaction stoichiometry is assumed to be valid at every instant during the reaction. This assumption is not always true. If the chemical reaction has intermediate species with lifetimes that enable their detection, then the stoichiometry is not time-independent, and the rate of the reaction cannot be defined in a unique way. In these cases, we are really talking about a sequence of chemical reactions, and ξ is a state variable for *each* chemical reaction in the sequence.

2.2 Experimental Rate Equation

Experimental studies show that the rates of many chemical reactions depend on the concentrations of the reactants according to the following equation:

$$v = k[A]^x[B]^y \quad (2.8)$$

where A and B are reactants, the exponents x and y are called **partial orders** of A and B, and k is called the **rate constant**. The **overall order** of the reaction is equal to $x + y$. Since k , x , y , and the concentrations in the second member of (2.8) are experimentally determined quantities, (2.8) is called the **experimental rate equation**. Partial orders x and y usually take the values 1, 2, or 0 (when the rate equation does not depend on the concentration of a particular reactant, its partial order with respect to that reactant is zero). Since the reaction rate depends on temperature, the experimental rate equation is *always* determined at a specified temperature.

Most chemical reactions have more than one reactant. When the partial order of one particular reactant is to be experimentally determined, conditions should be set to guarantee that other reactants do not interfere, and their concentrations will not vary significantly. For instance, considering a chemical reaction with reactants A and B, the experimental determination of the partial order of reactant A requires that [B] be kept approximately constant. Under these conditions, (2.8) takes the form

$$v = k'[A]^x \quad (2.9)$$

where $k' = k[B]^y \approx \text{constant}$, because [B] does not significantly change in the course of the reaction. Equation (2.9) is called the **pseudo rate equation**, and k' represents the **pseudo rate constant**. The partial order x acts like the overall pseudo-order for the chemical reaction. The isolation and initial rate methods allow separation of the concentration variables of a rate equation in order to determine the partial order of a particular reactant.

In the experimental determination of the partial order of A by the **isolation method**, the concentration of B should greatly exceed the initial concentration of A. If A and B are in the stoichiometric proportion 1:1 and the initial concentrations of A and B are in the ratio 1:100 (for example, $[A]_0 = 0.100 \text{ M}$ and $[B]_0 = 10.0 \text{ M}$), then when 99 % of A has reacted, the change in the concentration of B is only 1 %.

The **initial rate method** takes the rate equation at the initial instant ($t = 0$),

$$v_0 = k[A]_0^x[B]_0^y \quad (2.10)$$

The determination of the partial order of A requires kinetic experiments with different initial concentrations of A for the same initial concentration of B. For chemical reactions with products that decompose or interfere during the course of the reaction, the initial rate method is the sole method available for the kinetic study of such chemical reactions.

2.2.1 First-Order Reactions

The rate equation for a **first-order chemical reaction** with a single reactant (or a pseudo first-order chemical reaction) is given by

$$-d[A]/dt = k[A] \quad (2.11)$$

Solving this differential equation consists in finding the function $f(t) = [A]$ that satisfies (2.11) and the initial condition $f(0) = [A]_0$, where $[A]_0$ is the initial concentration of A. While it is easy to conclude that the function that satisfies (2.11) is an exponential [the derivative of $\exp(-kt)$ is $-k \exp(-kt)$], we solve (2.11) in a more general way that can be applied to second-order reactions. We begin by separating variables $[A]$ and t in each member,

$$d[A]/[A] = -kdt \quad (2.12)$$

Now we obtain indefinite integrals of both members. The integration limits for the first member are $[A]_0$ and $[A]$, and for the second member, are the corresponding values of time, that is, 0 and t . We obtain

$$\ln([A]/[A]_0) = -kt \quad (2.13)$$

This equation is equivalent to

$$\ln[A] = \ln[A]_0 - kt \quad (2.14)$$

that is, the graph of $\ln[A]$ as a function of t gives a straight line whose intercept is $\ln[A]_0$ and whose slope is equal to $-k$. If we now consider the time interval $t = t_{1/2}$ such that $[A]$ is half its initial value, $[A] = [A]_0/2$, then substitution of these equalities in (2.13) leads to

$$t_{1/2} = \ln 2/k \quad (2.15)$$

where the time interval $t_{1/2}$ is called the **half-life**. Contrary to what the name might suggest, the half-life is not half of the time to reaction completion. Equality (2.15), valid for first-order chemical reactions, shows that the half-life does not depend on $[A]_0$. This is an important result that applies *only* to first-order chemical reactions. Hence, when the half-life of a chemical reaction is independent of the initial concentration, we conclude that the chemical reaction has first-order kinetics (Fig. 2.2).

Equality (2.13) can be rewritten in the following equivalent way,

$$[A] = [A]_0 e^{-kt} \quad (2.16)$$

which shows that $[A]$ has **exponential decay** with time. Spontaneous decays of radioactive atomic nuclei are first-order processes. Adapting the above equalities to

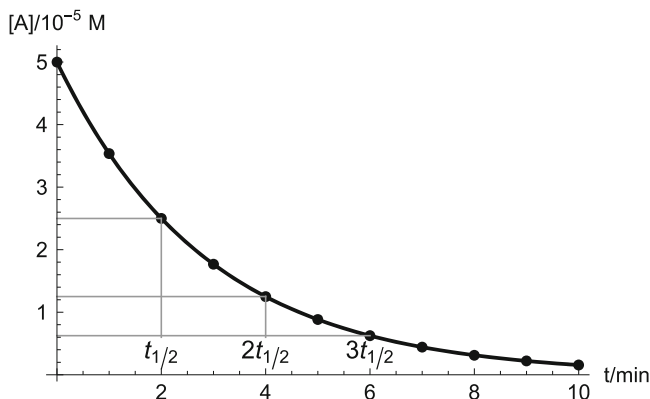


Fig. 2.2 The half-life of a first-order reaction does not depend on $[A]_0$. For the kinetic profile illustrated above, the half-life is approximately equal to 2 min. Figure obtained with *Mathematica*

radioactive decay simply requires substitution of $[A]$ by the number of radioactive nuclei N and of $[A]_0$ by N_0 . After these substitutions, Eq. (2.11) shows that the rate of radioactive decay ($-dN/dt$) is proportional to the number of nuclei that have not yet decayed (N). In radioactive studies, the half-life $t_{1/2}$ is preferred to the rate constant k , in contrast to what happens in chemical kinetics.

2.2.2 Second-Order Reactions

The rate equation for a second-order chemical reaction with a single reactant (or a pseudo second-order chemical reaction) is given by

$$-d[A]/dt = k[A]^2 \quad (2.17)$$

Separation of variables leads to

$$d[A]/[A]^2 = -kdt \quad (2.18)$$

After integration of both members, we obtain

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad (2.19)$$

Hence, the graph of $1/[A]$ as a function of t gives a straight line whose intercept is $1/[A]_0$ and whose slope is equal to k . Substitution of $[A]$ by $[A]_0/2$ and of t by $t_{1/2}$ in (2.19) gives the half-life for a second-order reaction:

$$t_{1/2} = \frac{1}{k[A]_0} \quad (2.20)$$

Hence, the half-life of a second-order reaction is inversely proportional to the initial concentration.

2.2.3 Zeroth-Order Reactions

Zeroth order with respect to a particular reactant means that the chemical reaction rate does not depend on the concentration of that reactant. This can occur when the reactant is not involved in the slowest step of the reaction (the rate-limiting or **rate-determining step**), or when the reaction rate depends on the adsorption of a particular reactant by a fully covered catalyst surface. Since the surface is saturated, the reaction rate does not depend on the concentration of the adsorbed reactant.

The rate equation of a zeroth-order chemical reaction for a single reactant is given by

$$-d[A]/dt = k[A]^0 = k \quad (2.21)$$

After separation of variables and integration of both members, we obtain

$$[A] = [A]_0 - kt \quad (2.22)$$

Thus, the graph of $[A]$ as a function of t gives a straight line whose intercept is $[A]_0$ and whose slope is equal to $-k$. Substitution of $[A]$ by $[A]_0/2$ and of t by $t_{1/2}$ in (2.22) leads to

$$t_{1/2} = [A]_0/(2k) \quad (2.23)$$

Hence, the half-life of a zeroth-order reaction is proportional to the initial concentration.

2.3 Effect of Temperature Change

The temperature-dependence of the rate of a chemical reaction lies essentially in the rate constant [see (2.8)], since the concentration factors expressed in molality are not affected by temperature (concentrations that involve a volume in their definition, like molarity, might be slightly affected by temperature variation). Based on observation of rate constant variations with temperature, Arrhenius (1859–1927; Nobel Prize in chemistry in 1903) proposed the $k(T)$ empirical, dependence given by

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2.24)$$

where E_a is the **Arrhenius activation energy** and A is the **Arrhenius A-factor (E3)**. The logarithm of (2.24) is

$$\ln k(T) = \ln A - \frac{E_a}{RT} \quad (2.25)$$

thus showing that $\ln k(T)$ depends linearly on $1/T$. The intercept of the resulting straight line is $\ln A$ and the slope is equal to $-E_a/R$. The derivative of (2.25) is given by

$$\frac{d \ln k(T)}{dT} = -\frac{E_a}{RT^2} \quad (2.26)$$

This equality suggests a way for determining the activation energy from experimental data on $k(T)$, provided the chemical reaction rate constant follows an Arrhenius dependence.

Above the troposphere, the stratosphere ranges in altitude from about 11–50 km, with temperature varying approximately from -60 to -2 °C. The ozone layer is mainly found in the lower layer of the stratosphere, up to an altitude of approximately 30 km. As an example of the Arrhenius dependence, consider the second-order stratospheric chemical reaction



for which $A = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E_a/R = 3600 \text{ K}$ (values taken from *Handbook of Chemistry and Physics*, 2011). The Arrhenius temperature-dependence of the rate constant of the above chemical reaction is illustrated in Fig. 2.3.

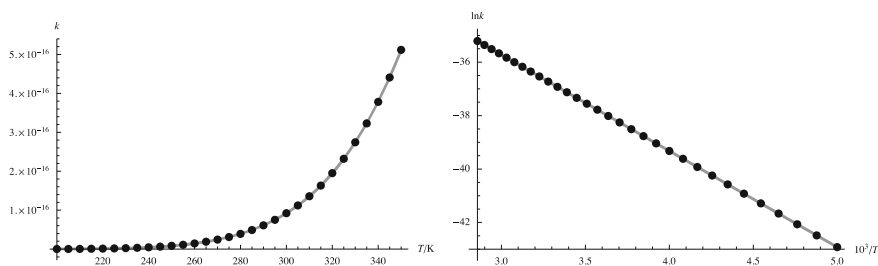


Fig. 2.3 Rate constant of the chemical reaction $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$ as a function of temperature (*left*), and $\ln k$ as a function of $10^3/T$ (*right*), in the temperature range from 200 to 350 K. Note that the lowest value of $10^3/T$ in the horizontal axis of the plot at the right is far from the origin, which would correspond to an infinite temperature. Thus, the intersection of the straight line with the horizontal axis is far from the intercept. Graphs obtained with *Mathematica*

$E_a/\text{kJ mol}^{-1}$	$\exp[-E_a/(RT)]$	
	300 K	600 K
10	2×10^{-2}	1×10^{-1}
50	2×10^{-9}	4×10^{-5}
100	4×10^{-18}	2×10^{-9}

The Arrhenius activation energy has a strong influence on the rate equation. To illustrate this point, the table shows approximate values of the Arrhenius exponential function for three hypothetical values of the activation energy (10, 50, and 100 kJ mol⁻¹), at two different temperatures (300 and 600 K). At 300 K, the Arrhenius exponential decreases by a factor of order 10⁻⁷ when the activation energy changes from 10 to 50 kJ mol⁻¹, and by a factor of order 10⁻⁹ when the activation energy changes from 50 to 100 kJ mol⁻¹. In turn, at 600 K, the same increments in the activation energy lead to exponential decreases by factors of order 10⁻⁴. In conclusion, the decrease in the activation energy due to the eventual use of catalysts and the increase in temperature lead to appreciable increases in the chemical reaction rates that present the Arrhenius dependence. Note that the catalyst reduces the activation energy of the chemical reaction, thus leading to an increase in the reaction rate. The decrease in the activation energy is the result of a change of mechanism without altering the initial and final states of the reaction (the reactants and products of the overall chemical reaction).

In the graph of $\ln k$ as a function of $10^3/T$ [see (2.25)], the extrapolation needed to obtain the intercept may lead to a large uncertainty in the determination of the A -factor, since the data points are usually within a short range of $10^3/T$. For instance, the data points of Fig. 2.3 range from $10^3/T = 2.85 \text{ K}^{-1}$ ($T \approx 351 \text{ K}$) to $10^3/T = 5.0 \text{ K}^{-1}$ ($T = 200 \text{ K}$). At 1000 K, the value of $10^3/T$ is 1 K^{-1} , still far from the origin.

2.4 Elementary Reactions

Elementary reactions occur in a single step and so have time-independent stoichiometries and do not have reaction intermediates. An elementary reaction has a single potential energy maximum in the reaction path as a function of the reaction coordinate. In contrast, the existence of one reaction intermediate in a chemical reaction implies an energy minimum in the reaction path between reactants and products.

Elementary reactions can be classified according to their **molecularity**, which is the number of reactant molecules that take part in the reaction. Those reactions that involve one, two, and, less frequently, three reactant molecules are called **uni-molecular**, **bimolecular**, and **trimolecular** reactions, respectively. There are few examples of chemical reactions thought to involve three reactant molecules, and no reactions are known to involve four reactant molecules, since it is highly

improbable that four molecules collide at the same instant with the energy and orientation required for a chemical reaction. Note that the term molecularity applies only to elementary reactions or to individual steps of complex reactions.

Consider a reaction of the following type:



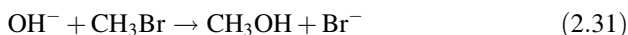
where Nu^- stands for a nucleophile and X represents an electronegative atom or an electronegative group bonded to a tetrahedral carbon atom in the R radical. A chemical reaction of this type is called a **nucleophilic substitution reaction**. In fact, it is a substitution reaction (X is substituted by Nu) resulting from a nucleophilic attack of Nu^- on the carbon atom bonded to X:



If the nucleophilic substitution reaction occurs in a single step, the approach of Nu^- is *concerted* with the withdrawal of X^- . In this case, the transition state involves both reactant species Nu^- and RX, and the nucleophilic substitution reaction is bimolecular and named $\text{S}_{\text{N}}2$. The reaction is said to occur in a **bi-molecular concerted step**, and its rate equation is given by

$$v = k[\text{RX}][\text{Nu}^-] \quad (2.30)$$

These considerations can be illustrated by the reaction of bromomethane with sodium hydroxide, in methanol, at 25 °C,



This reaction has second-order kinetics and obeys the following experimental rate equation:

$$v = k[\text{CH}_3\text{Br}][\text{OH}^-] \quad (2.32)$$

This reaction mechanism has a single step with a single transition state, $[\text{HO}\dots\text{CH}_3\dots\text{Br}]^-$. The transition state involves both reactant species, and the nucleophilic substitution is bimolecular, that is, the mechanism is $\text{S}_{\text{N}}2$.

2.5 Complex Reactions

When the mechanism of a chemical reaction consists of more than one step, the reaction is said to be a **complex reaction**. Experimental evidence for the existence of one reaction intermediate leads to the conclusion that the reaction mechanism is formed by at least two steps. Sometimes, the lifetime of a reaction intermediate enables its isolation and characterization. However, reaction intermediates usually are reactive species with

very low concentrations, thus being difficult to detect. The physical methods generally used in the detection of short-lived reaction intermediates are spectroscopic methods, which involve an interaction with electromagnetic radiation.

The rate equation of an elementary reaction can be written once the reaction stoichiometry is known. Hence, when the rate equation does not reflect the reaction stoichiometry, we have a complex reaction. For example, the reaction between hypochlorite and iodide ions in aqueous solution,

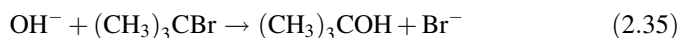


has the following experimental rate equation:

$$v = k[\text{ClO}^-][\text{I}^-]/[\text{OH}^-] \quad (2.34)$$

The presence of the concentration of the hydroxide ion in the rate equation and its absence from the stoichiometric Eq. (2.33) leads to the conclusion that the chemical reaction (2.33) has more than one step in its mechanism; that is, it is a complex reaction.

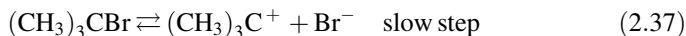
The reaction of 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, with sodium hydroxide, in methanol at 25 °C,



has the following experimental first-order rate equation:

$$v = k[(\text{CH}_3)_3\text{CBr}] \quad (2.36)$$

This rate equation shows that the slowest reaction step involves a single reactant species, namely, $(\text{CH}_3)_3\text{CBr}$. Having the chemical reaction (2.35) in mind, we can infer from (2.36) that the first step of (2.35) consists in the dissociation of $(\text{CH}_3)_3\text{CBr}$ in the $(\text{CH}_3)_3\text{C}^+$ carbocation and the bromide ion,



Considering the reactivity of the $(\text{CH}_3)_3\text{C}^+$ carbocation, it is likely that this chemical species recombines with the bromide ion to form 2-bromo-2-methylpropane, giving rise to an equilibrium. However, when the $(\text{CH}_3)_3\text{C}^+$ carbocation reacts with a hydroxide ion, an alcohol molecule is formed,



This is a fast step, because the hydroxide ion has a stronger nucleophilic character than the bromide ion. Addition of steps (2.37) and (2.38) brings back the original overall reaction (2.35). The transition state involves a single reactant molecule, $(\text{CH}_3)_3\text{CBr}$, and the overall reaction (2.35) represents a unimolecular nucleophilic substitution, thus being an example of an $\text{S}_{\text{N}}1$ mechanism.

The difference in the mechanisms of reactions (2.31) and (2.35) lies in the different stabilities of the involved carbocations, CH_3^+ and $(\text{CH}_3)_3\text{C}^+$. CH_3^+ is a stronger electrophile than $(\text{CH}_3)_3\text{C}^+$, because the same positive charge is distributed over a larger carbocation in $(\text{CH}_3)_3\text{C}^+$ as compared with CH_3^+ . Hence, reaction (2.31) does not have a slow initial step for the dissociation of CH_3Br into CH_3^+ and Br^- , since CH_3^+ is quite a strong electrophile for that to occur.

2.6 Extremely Fast Reactions

Most reactions of ions in aqueous solution are extremely fast, reaching equilibrium in times of order 10^{-10} and 10^{-12} s. Such reactions cannot be studied using conventional methods that depend on the mixture of reactants, since the diffusion times (times for migration of reactant molecules until they collide with each other) are orders of magnitude greater than reaction times. Techniques can be used that apply an almost instantaneous perturbation, after which the system momentarily leaves the equilibrium state (concentrations of reactants and products are changed for a moment) and returns to the equilibrium state, since the duration of the perturbation is not significant when compared with the reaction half-life. The process of returning to the equilibrium state is called **relaxation**. The applied perturbation can be a shock wave, a pulse of electromagnetic radiation that produces a photochemical reversible reaction (flash photolysis), a sudden temperature jump (T -jump), or a sudden pressure jump associated with sound absorption in gaseous systems (Eigen 1954). The study of extremely fast reactions using brief energy pulses led to the award of the 1967 Nobel Prize in chemistry to Manfred Eigen, Ronald Norrish, and George Porter.

In order to proceed with the study of an extremely fast chemical reaction, it is necessary to know the rate equation for the reaction in the forward and reverse directions. Consider the reaction in aqueous solution



where A and B are positive and negative ions and C is the chemical species resulting from the combination of those ions. Assume that the forward reaction is of first order in A and in B and that the reverse reaction is of first order in C, and represent by k_+ and k_- the rate constants in the forward and reverse reactions. When a brief perturbation, for instance a temperature jump, is applied to the reaction at equilibrium, the A, B, and C concentrations will change with respect to their equilibrium values according to the following equalities, which preserve the reaction stoichiometry:

$$[\text{A}] = [\text{A}]_{\text{eq}} - \delta \quad [\text{B}] = [\text{B}]_{\text{eq}} - \delta \quad [\text{C}] = [\text{C}]_{\text{eq}} + \delta \quad (2.40)$$

where δ represents an infinitesimal change in concentration caused by the perturbation. These equalities can be written in the following equivalent way:

$$\Delta[A] \equiv [A] - [A]_{\text{eq}} = -\delta \quad \Delta[B] \equiv [B] - [B]_{\text{eq}} = -\delta \quad \Delta[C] \equiv [C] - [C]_{\text{eq}} = \delta \quad (2.41)$$

Therefore, the relaxation rate satisfies the following equalities:

$$-\frac{d\Delta[A]}{dt} = -\frac{d\Delta[B]}{dt} = \frac{d\Delta[C]}{dt} = \frac{d\delta}{dt} \quad (2.42)$$

where, according to (2.39),

$$\frac{d\delta}{dt} = k_{\rightarrow}[A][B] - k_{\leftarrow}[C] \quad (2.43)$$

Substitution of (2.40) in (2.43) leads to

$$\frac{d\delta}{dt} = \alpha - \beta\delta + \chi\delta^2 \quad (2.44)$$

where

$$\alpha = k_{\rightarrow}[A]_{\text{eq}}[B]_{\text{eq}} - k_{\leftarrow}[C]_{\text{eq}} \quad \beta = k_{\rightarrow}([A]_{\text{eq}} + [B]_{\text{eq}}) + k_{\leftarrow} \quad \chi = k_{\rightarrow} \quad (2.45)$$

Since the equilibrium constant of (2.39) is given by

$$K_{\text{eq}} = \frac{k_{\rightarrow}}{k_{\leftarrow}} = \frac{[C]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}} \quad (2.46)$$

it follows that $\alpha = 0$. In addition, in (2.44), the second-order term in δ is negligible when compared with the first-order term. Therefore,

$$\frac{d\delta}{dt} \approx -\beta\delta \quad (2.47)$$

This result shows that the perturbation δ follows first-order kinetics,

$$\delta = \delta_0 e^{-\beta t} = \delta_0 e^{-t/\tau} \quad (2.48)$$

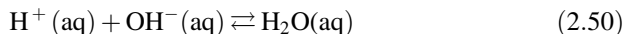
where

$$\beta = \tau^{-1} \quad (2.49)$$

(the units of β are the inverse of time, s^{-1}) (E4). The rate constants k_{\rightarrow} and k_{\leftarrow} can be experimentally determined if two values of β , say β_1 and β_2 , have been previously determined corresponding to two sets of $[A]_{\text{eq}}$ and $[B]_{\text{eq}}$ values (set₁ and set₂).

2.6.1 Neutralization Reaction in Water

Consider water and the neutralization equilibrium



where $\text{H}^+(\text{aq})$ stands for the symbolic representation of a protonated water molecule H_3O^+ or a protonated group of hydrogen-bonded water molecules as H_5O_2^+ , H_7O_3^+ , H_9O_4^+ , The rate constant for the combination of H^+ and OH^- is equal to $k_{\rightarrow} = 1.4 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, that is, the neutralization is an extremely fast reaction, whereas the rate constant for the reverse reaction (ionization of H_2O) is equal to $k_{\leftarrow} = 2.5 \times 10^{-5} \text{ s}^{-1}$ (Eigen 1967). At equilibrium, making use of (2.46), we can write

$$k_{\rightarrow}[\text{H}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}} - k_{\leftarrow}[\text{H}_2\text{O}] = 0 \quad (2.51)$$

where $[\text{H}_2\text{O}] \approx 55.6 \text{ mol dm}^{-3}$. Hence, the constant for the ionic product of water at 25 °C is given by

$$[\text{H}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}} = \frac{k_{\leftarrow}}{k_{\rightarrow}}[\text{H}_2\text{O}] = 1.0 \times 10^{-14} \quad (2.52)$$

that is, $[\text{H}^+]_{\text{eq}} = [\text{OH}^-]_{\text{eq}} = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$, at 25 °C.

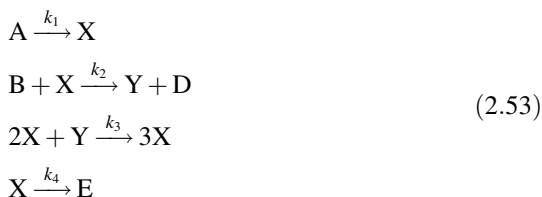
2.7 Chemical Oscillations

Most chemical reactions function like one-way streets: the concentrations of reactants decrease, those of reaction intermediates increase at first and decrease later, and the concentrations of products increase. However, for a few reactions far from equilibrium, the concentrations of some chemical species oscillate, i.e., increase and decrease repeatedly. These reactions are called **chemical oscillators**. Chemical oscillations differ from pendulum oscillations: the film of a pendulum cannot be distinguished from the same film run backward (there is no arrow of time in the pendulum), whereas chemical oscillators are associated with entropy production due to irreversible processes that occur in the reacting system.

The first reported observation of a periodic reaction in homogeneous solution is due to Bray in 1921 (Bray 1921). At that time, Lotka had reported the mathematical study of a system of differential equations describing the mechanism of a hypothetical periodic chemical reaction (Lotka 1920). The best-known oscillating chemical reaction results from experiments carried out by Belousov in 1958 and by Zhabotinsky in 1964, and is known as the **Belousov–Zhabotinsky experiment** (Winfree 1984). For years, the results of the Belousov–Zhabotinsky experiment were regarded with suspicion, since oscillations are incompatible with the existence of a Gibbs energy minimum at equilibrium. This apparent incompatibility was resolved when it was realized that chemical oscillations occur far from equilibrium.

2.7.1 Brusselator

In 1968, Prigogine and Lefever developed a model that shows how a chemical reaction, far from equilibrium, can pass from a stationary point to an oscillatory state (Prigogine 1968). This chemical oscillator, often called the **Brusselator** as a reminder of the Brussels thermodynamic school founded by Prigogine, consists of the following mechanism:



where the inverse reactions are assumed to have negligible rate constants, and the overall chemical reaction is



In order to simplify the notation, A , B , X , and Y stand for $[A]$, $[B]$, $[X]$, and $[Y]$, respectively. Note that an increase of X , in elementary reactions 1 and 3, is followed by its decrease, in chemical reactions 2 and 4. A similar oscillatory behavior can be assigned to Y that decreases in chemical reaction 3, where Y is a reactant, and increases in reaction 2, where Y is a product.

The rate equations for the reaction intermediates X and Y in (2.53) are given by the following set of nonlinear coupled differential equations:

$$\frac{dX}{dt} = k_1A - k_2BX + k_3X^2Y - k_4X \quad \frac{dY}{dt} = k_2BX - k_3X^2Y \tag{2.55}$$

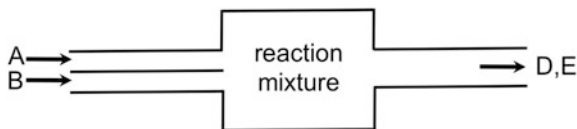


Fig. 2.4 In a flow reactor, the constant supply of A and B keeps the concentrations of these reactants in the reaction mixture fixed, and the constant removal of D and E maintains the system far from these reactants equilibrium

where the effects of diffusion of X and Y have been ignored, since we assume that chemical reactions (2.53) occur in a homogeneous medium, and so there is spatial uniformity of concentrations of all involved chemical species. In solving this set of nonlinear differential equations, the initial conditions are such that the corresponding physical system (the reaction mixture) is kept far from equilibrium: A and B have fixed values, while D and E are constantly removed from the reaction mixture to prevent reverse chemical reactions from occurring (Fig 2.4). Solving (2.55) for its stationary-point solutions ($dX/dt = 0$ and $dY/dt = 0$) leads to

$$X_s = \frac{k_1}{k_4} A \quad Y_s = \frac{k_2 k_4 B}{k_1 k_3 A} \quad (2.56)$$

where the subscript s stands for **stationary point**.

In order to assess the linear stability of the stationary point, we consider a time-dependent perturbation added to the stationary point solutions (2.56) and find out whether the perturbation increases or decreases in time (see *Kondepudi and Prigogine*, Further Reading).

The rate Eq. (2.55) can be written in the following more general way:

$$\frac{dX}{dt} = Z_1(X, Y) \quad \frac{dY}{dt} = Z_2(X, Y) \quad (2.57)$$

The time-dependent perturbations $x(t)$ and $y(t)$ are added to the stationary-point coordinates X_s and Y_s ,

$$X = X_s + x(t) \quad Y = Y_s + y(t) \quad (2.58)$$

Therefore,

$$\frac{dX}{dt} = \frac{dx}{dt} \quad \frac{dY}{dt} = \frac{dy}{dt} \quad (2.59)$$

since X_s and Y_s are constants of the experiment. The Taylor expansion of Z_1 and Z_2 in (2.57) about the stationary point leads to

$$\begin{aligned}
Z_1(X_s + x, Y_s + y) &= Z_1(X_s, Y_s) + \left(\frac{\partial Z_1}{\partial X}\right)_s x + \left(\frac{\partial Z_1}{\partial Y}\right)_s y + \dots \\
Z_2(X_s + x, Y_s + y) &= Z_2(X_s, Y_s) + \left(\frac{\partial Z_2}{\partial X}\right)_s x + \left(\frac{\partial Z_2}{\partial Y}\right)_s y + \dots
\end{aligned} \tag{2.60}$$

Since $x(t)$ and $y(t)$ represent small perturbations, only the linear terms in (2.60) are retained (quadratic and higher-order terms are ignored). Hence, making use of (2.57) and (2.59), and noting that $Z_1(X_s, Y_s)$ and $Z_2(X_s, Y_s)$ are zero by definition of the stationary point, we conclude that

$$\frac{dx}{dt} = \left(\frac{\partial Z_1}{\partial X}\right)_s x + \left(\frac{\partial Z_1}{\partial Y}\right)_s y \quad \frac{dy}{dt} = \left(\frac{\partial Z_2}{\partial X}\right)_s x + \left(\frac{\partial Z_2}{\partial Y}\right)_s y \tag{2.61}$$

or in vector notation,

$$\frac{d\mathbf{x}}{dt} = \Lambda \mathbf{x} \tag{2.62}$$

where

$$\Lambda = \begin{bmatrix} \left(\frac{\partial Z_1}{\partial X}\right)_s & \left(\frac{\partial Z_1}{\partial Y}\right)_s \\ \left(\frac{\partial Z_2}{\partial X}\right)_s & \left(\frac{\partial Z_2}{\partial Y}\right)_s \end{bmatrix} \quad \mathbf{x} = \begin{pmatrix} x \\ y \end{pmatrix} \tag{2.63}$$

with Λ being the **Jacobian matrix**. The Jacobian matrix elements quantify the variation of the Z_1 and Z_2 rates with respect to changes in X and Y at the stationary point.

For the Brusselator, the Jacobian matrix is given by

$$\Lambda = \begin{pmatrix} k_2 B - k_4 & k_3 X_s^2 \\ -k_2 B & -k_3 X_s^2 \end{pmatrix} \tag{2.64}$$

where X_s is given by the first equality of (2.56). The **characteristic equation** (see §1) is

$$\det(\Lambda - \lambda I) = 0 \tag{2.65}$$

that is,

$$\begin{vmatrix} k_2 B - k_4 - \lambda & k_3 X_s^2 \\ -k_2 B & -k_3 X_s^2 - \lambda \end{vmatrix} = 0 \quad \lambda^2 - (k_2 B - k_4 - k_3 X_s^2)\lambda + k_3 k_4 X_s^2 = 0 \tag{2.66}$$

The eigenvalues λ_{\pm} are obtained by solving Eq. (2.66),

$$\lambda_{\pm} = \frac{p}{2} \pm \frac{1}{2}(p^2 - 4q)^{1/2} \quad (2.67)$$

where

$$p = k_2B - k_4 - k_3X_s^2 \quad q = k_3k_4X_s^2 \quad (2.68)$$

(E5).

Consider now the following set of parameters $k_1 = k_2 = k_3 = k_4 = 1.0$ and the initial condition $A = 1.0$, leading to $X_s = 1.0$, $Y_s = B$ [see (2.56)], $p = B - 2$, $q = 1$ [see (2.68)], and $p^2 - 4q = B^2 - 4B$. For $B = 2$, we have $p = 0$, and the eigenvalues of the Jacobian matrix are pure imaginary. For $B = 1.5$ or 2.5 , we have $p^2 - 4q = (\pm 0.5)^2 - 4 < 0$, and the eigenvalues have a nonzero imaginary part. The value $B = 1.5$ leads to $p < 0$ and to a complex conjugate pair with a negative real part, whereas $B = 2.5$ gives $p > 0$ and a positive real part. We now return to the initial conditions $A = 1.0$ and $B = 2$. From (2.62) and (2.64), we can write

$$\begin{pmatrix} \dot{x}(t) \\ \dot{y}(t) \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ -2 & -1 \end{pmatrix} \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} \quad (2.69)$$

The eigenvalues of this Jacobian matrix are $\pm i$, and the corresponding eigenvectors are $(-1 - i, 2)^T$ and $(-1 + i, 2)^T$. Then the general solution to the above system of differential equations (see §2) is

$$\begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = c_1 \begin{pmatrix} -1 - i \\ 2 \end{pmatrix} e^{it} + c_2 \begin{pmatrix} -1 + i \\ 2 \end{pmatrix} e^{-it} \quad (2.70)$$

After applying $e^{\pm it} = \cos t \pm i \sin t$, we obtain

$$\begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \cos t + \begin{pmatrix} \chi \\ \delta \end{pmatrix} \sin t \quad (2.71)$$

This equality shows that the $x(t)$ and $y(t)$ functions are linear combinations of cosine and sine functions. We now define U and V variables by $U \equiv X - X_s$ and $V \equiv Y - Y_s$, so that the stationary point is at $(U_s, V_s) = (0, 0)$ instead of at (X_s, Y_s) . Figure 2.5 considers the same set of parameters ($k_1 = k_2 = k_3 = k_4 = 1.0$) and the initial condition $A = 1.0$, with B equal to 1.5, 2.0, and 2.5, and shows U and V as functions of time in the first plot and $V(t)$ as a function of $U(t)$ in the second plot (**phase trajectory**). For $B = 1.5$, the eigenvalues of the Jacobian matrix are a

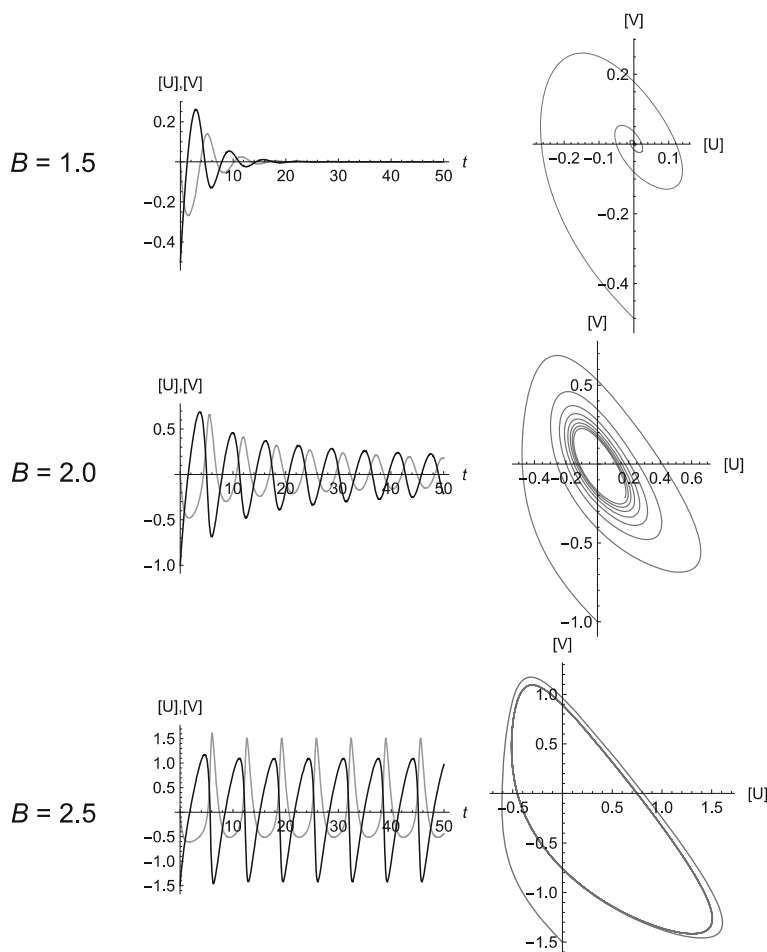


Fig. 2.5 Oscillations and phase trajectories for the Brusselator. Figures obtained with *Mathematica*

complex conjugate pair with a negative real part, and U and V quickly decay to zero as the phase trajectories rapidly spiral into the origin. For $B = 2.0$, the eigenvalues of Jacobian matrix are pure imaginary, and the trajectories spiral asymptotically to the origin as $t \rightarrow \infty$ (see *Mathematica* code **M2**). In turn, when $B = 2.5$, the eigenvalues of the Jacobian matrix are a complex conjugate pair with a positive real part, and the trajectories quickly approach a stable limit cycle as $t \rightarrow \infty$, with $U(t)$ and $V(t)$ indefinitely maintaining the same amplitudes and same shapes (the system is said to have reached permanent oscillations) (**E6**).

Notes

§1. Matrix Diagonalization

When a linear transformation represented by an $n \times n$ matrix A is applied to a vector \mathbf{u} represented by an $n \times 1$ column vector, another $n \times 1$ vector \mathbf{w} of the same vector space is obtained according to the following equation:

$$A\mathbf{u} = \mathbf{w} \quad (2.72)$$

This equality represents a linear transformation within the same vector space, which is said to preserve the vector length, since \mathbf{u} and \mathbf{w} have the same length. One especial and very important case of (2.72) quite frequent in quantum mechanics occurs when the vector \mathbf{w} is equal to a scalar λ times the column vector \mathbf{u} , that is,

$$A\mathbf{u} = \lambda\mathbf{u} \quad (2.73)$$

where the scalar λ and the vector \mathbf{u} are to be determined (they are not known beforehand). Certainly, the trivial solution $\mathbf{u} = \mathbf{0}$ is of no practical interest! Values of λ and nontrivial vectors \mathbf{u} that satisfy (2.73) are called **eigenvalues** and **eigenvectors**, respectively. Equality (2.73) can be rewritten as

$$(A - \lambda I)\mathbf{u} = \mathbf{0} \quad (2.74)$$

where the expression in parentheses is an $n \times n$ matrix. The equality (2.74) represents a homogeneous system of linear equations in n unknowns, and so the condition for a nontrivial solution of (2.74) is

$$\det(A - \lambda I) = |A - \lambda I| = 0 \quad (2.75)$$

Expansion of this determinant yields an n th-degree polynomial in λ . The polynomial Eq. (2.75) is called the **characteristic equation** or **secular equation**. The n roots of the characteristic equation are the n eigenvalues that satisfy (2.75). Substitution of each of these eigenvalues in (2.74) enables one to determine the corresponding eigenvector only to within a multiplicative constant, because if \mathbf{u} is a solution of (2.74), so is any multiple of \mathbf{u} .

We can now illustrate the above considerations with the matrix

$$A = \begin{pmatrix} 1 & 0 & -1 \\ 1 & 2 & 1 \\ 2 & 2 & 3 \end{pmatrix} \quad (2.76)$$

The characteristic equation is

$$\det(A - \lambda I) = \begin{vmatrix} 1 - \lambda & 0 & -1 \\ 1 & 2 - \lambda & 1 \\ 2 & 2 & 3 - \lambda \end{vmatrix} = -(\lambda - 3)(\lambda - 2)(\lambda - 1) = 0 \quad (2.77)$$

whose roots are $\lambda = 1, 2, 3$. We obtain the following eigenvectors:

$$\lambda = 1 \Rightarrow (A - I)\mathbf{u}_1 = \begin{pmatrix} 0 & 0 & -1 \\ 1 & 1 & 1 \\ 2 & 2 & 2 \end{pmatrix} \mathbf{u}_1 = 0 \Rightarrow \mathbf{u}_1 = a \begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix} \quad (2.78)$$

$$\lambda = 2 \Rightarrow (A - 2I)\mathbf{u}_2 = \begin{pmatrix} -1 & 0 & -1 \\ 1 & 0 & 1 \\ 2 & 2 & 1 \end{pmatrix} \mathbf{u}_2 = 0 \Rightarrow \mathbf{u}_2 = b \begin{pmatrix} -2 \\ 1 \\ 2 \end{pmatrix} \quad (2.79)$$

$$\lambda = 3 \Rightarrow (A - 3I)\mathbf{u}_3 = \begin{pmatrix} -2 & 0 & -1 \\ 1 & -1 & 1 \\ 2 & 2 & 0 \end{pmatrix} \mathbf{u}_3 = 0 \Rightarrow \mathbf{u}_3 = c \begin{pmatrix} -1 \\ 1 \\ 2 \end{pmatrix} \quad (2.80)$$

The multiplicative constants a , b , and c can be determined once the lengths of \mathbf{u}_1 , \mathbf{u}_2 , \mathbf{u}_3 are known. The eigenvectors \mathbf{u}_1 , \mathbf{u}_2 , \mathbf{u}_3 can be grouped as columns of a 3×3 matrix U , and the eigenvalues can be arranged as diagonal entries of the diagonal matrix D ,

$$U = \begin{pmatrix} | & | & | \\ \mathbf{u}_1 & \mathbf{u}_2 & \mathbf{u}_3 \\ | & | & | \end{pmatrix} \quad D = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \quad (2.81)$$

Using (2.74) for each of the eigenvalues λ_1 , λ_2 , and λ_3 , we can write

$$\begin{aligned} AU &= (A\mathbf{u}_1, A\mathbf{u}_2, A\mathbf{u}_3) = (\lambda_1\mathbf{u}_1, \lambda_2\mathbf{u}_2, \lambda_3\mathbf{u}_3) \begin{pmatrix} | & | & | \\ \mathbf{u}_1 & \mathbf{u}_2 & \mathbf{u}_3 \\ | & | & | \end{pmatrix} \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \\ &= UD \end{aligned} \quad (2.82)$$

Note that the product UD gives each eigenvalue corresponding to a column of the resulting matrix, as we want. On the other hand, the product DU would give each eigenvalue corresponding to a row of the product matrix. Considering (2.82), we can write

$$AU = UD \quad (2.83)$$

If the eigenvectors are linearly independent, then U is nonsingular, that is, its determinant is different from zero. Therefore, U^{-1} exists, and we can multiply (2.83) from the left by U^{-1} and obtain

$$U^{-1}AU = D \quad (2.84)$$

Two $n \times n$ matrices A and B are called **similar** if $B = X^{-1}AX$ for some nonsingular and therefore invertible matrix X . The transformation $A \rightarrow X^{-1}AX$ is a **similarity transformation**. Similar matrices represent the same transformation (operator) in two different bases of the same vector space related by the matrix X . Equality (2.84) shows a particular kind of a similarity transformation, whose result is a diagonal matrix. For that reason, (2.84) represents the **diagonalization** of the matrix A . The similarity transformation that diagonalizes the matrix A linearly combines the basis vectors, so that the resulting matrix becomes diagonal in the new basis.

We now illustrate the concepts of similarity transformation and similar matrices using a three-dimensional vector space with Cartesian coordinates and the basis vectors $(xyz)^T$ and $(rst)^T$. Consider the 3×3 matrix A that converts $(xyz)^T$ into $(x'y'z')^T$,

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = A \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (2.85)$$

and the 3×3 matrix B that converts $(rst)^T$ into $(r's't')^T$,

$$\begin{pmatrix} r' \\ s' \\ t' \end{pmatrix} = B \begin{pmatrix} r \\ s \\ t \end{pmatrix} \quad (2.86)$$

Matrix X relates these bases: by applying the matrix X to $(rst)^T$ and $(r's't')^T$, we obtain $(xyz)^T$ and $(x'y'z')^T$, respectively,

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = X \begin{pmatrix} r \\ s \\ t \end{pmatrix} \quad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = X \begin{pmatrix} r' \\ s' \\ t' \end{pmatrix} \quad (2.87)$$

The change of basis can be carried in the opposite direction, from $(xyz)^T$ and $(x'y'z')^T$ to $(rst)^T$ and $(r's't')^T$, meaning that X^{-1} exists, that is, X is nonsingular (its determinant is different from zero). If X is a symmetry operation, then as an element of an algebraic group, it has an inverse. Therefore, substitution of (2.87) in (2.85) gives

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = A \begin{pmatrix} x \\ y \\ z \end{pmatrix} \Rightarrow X \begin{pmatrix} r' \\ s' \\ t' \end{pmatrix} = AX \begin{pmatrix} r \\ s \\ t \end{pmatrix} \Rightarrow \begin{pmatrix} r' \\ s' \\ t' \end{pmatrix} = X^{-1}AX \begin{pmatrix} r \\ s \\ t \end{pmatrix} \quad (2.88)$$

Comparison of this result with (2.86) leads to

$$B = X^{-1}AX \quad (2.89)$$

where $X^{-1}AX$ is called a **similarity transformation** and A and B are said to be **similar matrices**, that is, they represent the same linear transformation after a change of basis implemented by the matrix X . If both coordinate systems are orthogonal, then the inverse of matrix X is equal to its transpose, that is,

$$X^{-1} = X^T \quad (2.90)$$

The matrix X is said to be **orthogonal**, and X^TAX is called an **orthogonal transformation**. An important conclusion about changing the vectorial basis within the same vector space is that a similarity transformation preserves the sum of the diagonal elements or trace of matrices A and B .

§2. Systems of First-Order Linear Differential Equations

Consider the system of two simultaneous first-order linear equations that corresponds to (2.62),

$$\dot{\mathbf{x}} = \Lambda \mathbf{x} \quad (2.91)$$

Since this system of differential equations has constant coefficients, it is reasonable to expect that a solution might be of the form

$$\mathbf{x}(t) = \mathbf{u}e^{\lambda t} \quad (2.92)$$

where \mathbf{u} and λ are to be determined. Substitution of (2.92) into (2.91) and cancellation of $e^{\lambda t}$ from both sides gives the eigenvalue equation

$$\Lambda \mathbf{u} = \lambda \mathbf{u} \quad (2.93)$$

Since (2.91) is a system of *linear* differential equations, if $\mathbf{x}_1(t)$ and $\mathbf{x}_2(t)$ are solutions, then

$$\mathbf{x}(t) = c_1\mathbf{x}_1(t) + c_2\mathbf{x}_2(t) \quad (2.94)$$

is also a solution. Therefore, from (2.92) and (2.94) we conclude that the general solution for (2.91) is given by

$$\mathbf{x}(t) = c_1\mathbf{u}_1e^{\lambda_1 t} + c_2\mathbf{u}_2e^{\lambda_2 t} \quad (2.95)$$

where \mathbf{u}_1 and \mathbf{u}_2 are eigenvectors and λ_1 and λ_2 are the corresponding eigenvalues (see McQuarrie, Sect. 11.6, p. 563).

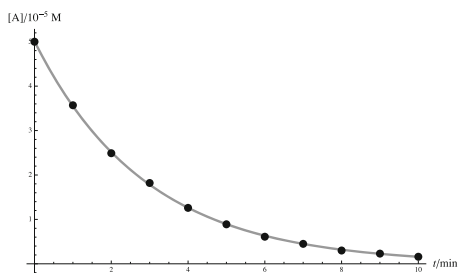
Mathematica Codes

M1. First-Order Chemical Reaction

```
data={{0.,5.00},{1.,3.57},{2.,2.49},{3.,1.82},{4.,1.26},{5.,0.89},{6.,0.61},{7.,0.45},
      {8.,0.30},{9.,0.23},{10.,0.16}};
model=a Exp[-k t];
fit=FindFit[data,model,{a,k},t]
f=Function[t,Evaluate[model/.fit]]
Plot[f[t],{t,0,10},PlotStyle->{Gray,Thickness[0.006]},
     AxesLabel->{Style["t/min",FontSize->14,Black],Style["[A]/10-5 M",FontSize->14,Black]},
     Epilog->{PointSize[0.020],Black,Map[Point,data]},ImageSize->{550,350}]

{a->5.01042,k->0.344655}

Function[t,5.01042 e-0.344655 t]
```



This *Mathematica* code does a least squares fit of kinetic data to a model of exponential decay and plots the resulting exponential function and the kinetic data points. The first line of code presents a list of data points named *data*, and the second line defines the model of exponential decay

```
model=a Exp[-k t];
```

In turn, the third line of code,

```
fit=FindFit[data,model,{a,k},t]
```

does the fitting, where the command *FindFit* finds a least squares fit for the defined model function, and the second line of results presents the function

```
Function[t,5.01042 e-0.344655 t]
```

where the comma inside square brackets separates the time variable *t* from the body of the pure function

$$5.01042 e^{-0.344655 t}$$

The function *f[t]* is plotted in the last line of code, and the data points are rendered over the plotted curve by the *Mathematica* command *Epilog*, whose main action is

```
Map[Point,data]
```

This *Mathematica* function *Map* applies *Point* to each element of *data*.

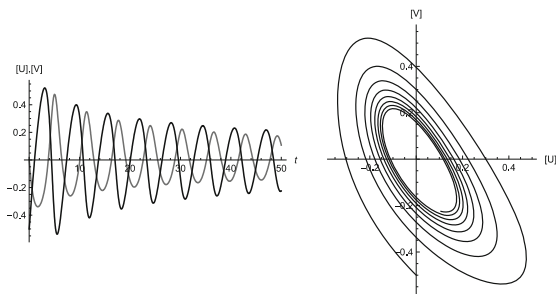
Suggestion: Complete the code to evaluate the half-life to a precision of four decimal places.

M2. Brusselator

```

k1=1.0; k2=1.0; k3=1.0; k4=1.0;
A=1.0; B=2.0;
u0=0.0; v0=-0.5;
a=1.0; b=2.0;
mt=50; ms=10000;
sol=NDSolve[{U'[t]==k1 A-k2 B(U[t]+a)+k3 (V[t]+b) (U[t]+a)^2-k4 (U[t]+a),
V'[t]==k2 B(U[t]+a)-k3 (V[t]+b) (U[t]+a)^2,U[0]==u0,V[0]==v0},
{U,V},{t,0,mt},MaxSteps->ms];
Row[{Plot[Evaluate[{U[t],V[t]}/.sol],{t,0,mt},AxesLabel->{"t","[U]","[V]"},AxesStyle->
Directive[FontFamily->"Arial",FontSize->10],PlotStyle->{{Thickness[0.006],Darker[Gray]}},
{Thickness[0.006],Black}},PlotRange->All,ImageSize->{300,300}],
ParametricPlot[Evaluate[{U[t],V[t]}/.sol],{t,0,mt},AxesLabel->{"[U]","[V]"},
AxesStyle->Directive[FontFamily->"Arial",FontSize->10],
PlotStyle->{Black,Thickness[0.006]},PlotRange->All,ImageSize->{300,300}]}]

```



This *Mathematica* code solves the equations of the Brusselator for $k_1 = k_2 = k_3 = k_4 = 1.0$, $A = 1.0$, and $B = 2.0$. Representing by $X(t)$ and $Y(t)$ the concentrations of the intermediates as functions of time and by X_s and Y_s the corresponding stationary values [for the above set of parameters, $X_s = 1.0$ and $Y_s = 2.0$, see (2.56)], the variables U and V are such that $X = U + X_s$ and $Y = V + Y_s$ and the rate equations are solved using the *Mathematica* command *NDSolve*, which finds a numerical solution for ordinary differential equations like the rate equations of the Brusselator [see (2.55)].

The last line of code plots in a row the $U(t)$ and $V(t)$ functions in the same graph and V as a function of U (a parametric plot) in a second graph. Removing from the last code line all the plot style options, we obtain

```

Row[{Plot[Evaluate[{U[t],V[t]}/.sol],{t,0,mt}],
ParametricPlot[Evaluate[{U[t],V[t]}/.sol],{t,0,mt}]}]

```

where the *Mathematica* function *Evaluate* causes $\{U[t],V[t]\}/.sol$ to be evaluated, that is, $U[t]$ and $V[t]$ are replaced by the solutions of the rate equations *sol*. Note that the opposite of *Evaluate* is *Hold*, which maintains an expression to which it applies in an unevaluated form. *ParametricPlot* generates a plot of V as a function of U , since both of these variables are functions of time, an external variable, or parameter.

For the above-mentioned initial conditions ($k_1 = k_2 = k_3 = k_4 = 1.0$, $A = 1.0$, and $B = 2.0$), the eigenvalues of the Jacobian matrix are pure imaginary [$p = 0$ and

$q = 1$; see (2.67) and (2.68)], and the trajectories spiral asymptotically to the origin as $t \rightarrow \infty$, as can be concluded by inspection of the phase trajectory shown above.

Suggestion: Using the *Mathematica* function `Table`, write a *Mathematica* code for solving the equations of the Brusselator for $k_1 = k_2 = k_3 = k_4 = 1.0$, $A = 1.0$, and three values of B , namely, $B = 1.5$, 2.0 , and 2.5 .

Glossary

Arrhenius equation	The empirical exponential dependence of the rate constant as a function of temperature, proposed by Arrhenius (1859–1927; Nobel Prize in chemistry in 1903); see (2.24). Contains two empirical parameters, the Arrhenius A -factor and the Arrhenius activation energy E_a .
Belousov–Zhabotinsky experiment	The best-known oscillating chemical reaction, resulting from experiments carried out by Belousov in 1958 and Zhabotinsky in 1964. For years, the results of this experiment were regarded with suspicion, since oscillations are incompatible with the existence of a Gibbs energy minimum at equilibrium. This apparent incompatibility was solved when it was realized that chemical oscillations occur far from equilibrium.
Brusselator	A model chemical oscillator developed in 1968 by Prigogine and Lefever, in the Brussels thermodynamic school founded by Prigogine, that shows how a chemical reaction, far from equilibrium, can pass from a stationary point to an oscillatory state; see (2.53).
Chemical oscillator	A complex reaction in which, far from equilibrium, the concentrations of some chemical species oscillate, i.e., increase and decrease repeatedly.
Complex reaction	A chemical reaction whose mechanism consists of more than one step, with the slowest step being the rate-determining step. When existing experimental evidence points to the occurrence of one reaction intermediate, then one can conclude that the reaction mechanism is formed by at least two steps.

Elementary reaction	A chemical reaction that occurs in a single step, has a time-independent stoichiometry, and does not have any reaction intermediate. An elementary reaction has a single potential energy maximum in the reaction path as a function of the reaction coordinate.
Extremely fast reaction	A chemical reaction that reaches equilibrium in times of order 10^{-10} and 10^{-12} s and so cannot be studied using conventional methods that depend on the mixture of reactants, since the diffusion times (times for migration of reactant molecules until they collide with each other) are orders of magnitude greater than the above reaction times.
Half-life	The time interval required for the concentration of a reactant or the number of radioactive atoms to decrease to half its initial value.
Initial rate method	Involves measuring the reaction rate of a chemical reaction at very short times before any significant changes in the concentrations of reactants occur; see (2.10).
Isolation method	Involves measuring the reaction rate of a chemical reaction when the concentration of one reactant is greatly exceeded by the concentrations of all other reactants so that these do not significantly change during the reaction. Under these conditions, the rate equation takes a much simpler form with a pseudo rate constant; see (2.9) and compare with (2.8).
Kinetic reaction profile	The graphical representation of the concentration of a reactant or product of a chemical reaction as a function of time.
Overall reaction order	The sum of all partial orders in the experimental rate equation.
Partial order	The exponent to which the concentration of a reactant is raised in the experimental rate equation. For many chemical reactions, the partial orders are not equal to the reaction stoichiometric coefficients, whereas for elementary chemical reactions, partial orders coincide with the stoichiometric coefficients.
Rate of chemical reaction	The time derivative of the concentration of a reactant or product of a chemical reaction divided by the corresponding stoichiometric number; see (2.7).

Exercises

E1. Considering the experimental data that led to Fig. 2.1, use *Mathematica* to calculate the rate constant for the first-order chemical reaction and the time elapsed until the concentration of A is reduced to 5 % of its initial value.

E2. Derive (2.7).

E3. For a second-order chemical reaction and the following rate constant values, use *Mathematica* for determining the Arrhenius activation energy.

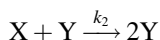
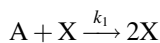
T/K	900	950	1000	1050	1100	1150
$k/\text{M}^{-1} \text{s}^{-1}$	0.01305	0.07686	0.37907	1.60593	5.96669	19.7777

E4. Derive (2.44).

E5. Consider the Brusselator.

- Write the set of differential equations for the concentrations of X and Y as functions of time and determine the stationary point.
- Obtain the Jacobian matrix at the stationary point. Assume $k_1 = k_2 = k_3 = k_4 = 1.0$ and $A = 1.0$, and determine the Jacobian matrix in terms of B .
- Use *Mathematica* for determining the eigenvalues of the Jacobian matrix for $B = 2.0$.

E6. Consider the Lotka–Volterra mechanism



- Write the set of differential equations for the concentrations of X and Y as functions of time and determine the stationary point.
- Determine the Jacobian matrix at the stationary point. Assume $k_1 = k_2 = k_3 = 1$ and $A = 1.0$ and determine the Jacobian matrix for these values.
- Use *Mathematica* for determining the eigenvalues of the Jacobian matrix.
- Use *Mathematica* for solving the kinetic equations, plot $U(t)$, $V(t)$, and the phase trajectory.

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