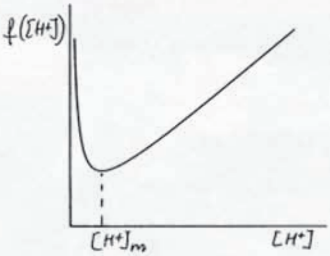
Mathematical Problems for Chemistry Students

György Póta



$$\lim_{[H^+]\to 0} f([H^+]) = \lim_{[H^+]\to \infty} f([H^+]) = \infty$$

$$\frac{df}{d[H^+]}([H^+]_m) = 1 - \frac{K_w}{[H^+]_m^2} = 0$$

$$\frac{d^2f}{d[H^+]^2}([H^+]) = \frac{2K_w}{[H^+]^3} > 0$$

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Preface

This problem collection has been compiled and written: (a) to help chemistry students in their mathematical studies by providing them with mathematical problems really occurring in chemistry, (b) to help practising chemists to activate their applied mathematical skills, and (c) to introduce students and specialists of the chemistry-related fields (physicists, mathematicians, biologists, etc.) into the world of the chemical applications.

Some problems of the collection are mathematical reformulations of those in the standard textbooks of chemistry, others were taken from theoretical chemistry journals, keeping in mind that the chemical considerations and the mathematical tools in the problems cannot be inaccessible or boring for the students. There are several original problems as well. All major fields of chemistry are covered, and relatively new results, like those related to multistability, chemical oscillations and waves are also included. Each problem is given a solution.

The collection is intended for beginners and users at an intermediate level. Although these properly formulated mathematical problems can be solved without a detailed knowledge of chemistry, we would also like to generate some interest in the chemical backgrounds of the problems. Almost each problem contains a reference in which the chemical details can be found.

The collection can be used as a companion to virtually all textbooks dealing with scientific and engineering mathematics or specifically mathematics for chemists. A few problems may require special tools but these are referenced in the given problem or are supplied in the appendix.

For mainly pedagogical reasons, the assertions and proofs sometimes differ from those in the original works. Any inconsistency or mistake in the material of the book is solely my responsibility.

I wish to thank the Department of Chemistry and the Department of Mathematics of the University of Debrecen for giving me the opportunity to take part in the mathematical training of chemistry students. I am grateful to the staff of the Department of Chemistry, especially Professor Vilmos Gáspár, for their valuable advice and help. I am indebted to Mr. István Vida for his remarks on the text. I owe thanks to my family for their patience and support.

Balancing on the border of two sciences is a difficult, somewhat dangerous but a joyful enterprise.

I wish the readers of this book good work and fun, and kindly ask them to send their remarks to me (e-mail address: potagy@delfin.unideb.hu).

Debrecen December 2005
György Póta

Chapter 1

Problems

1.1 ALGEBRA

1. The Hermite polynomials [1, 2, p. 60] play an important role in the description of the vibrational motion of the molecules [3, p. 476]. The first few Hermite polynomials are given in Table 1.1 ($-\infty < x < \infty$), and each question in this problem concerns these polynomials.
   (a) Confirm by direct calculation that the general relationship

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x)$$

   is valid for the polynomials.
   (b) Which polynomials are even functions and which are odd ones?
   (c) Which are the polynomials whose zeros include 0?
   (d) Which are the polynomials whose real zeros are symmetrical to the origin?
   (e) Which polynomials can have an even number of real zeros? Why?

Table 1.1 The first few Hermite polynomials

n	$H_n(x)$
0	1
1	$2x$
2	$4x^2 - 2$
3	$4x(2x^2 - 3)$
4	$4(4x^4 - 12x^2 + 3)$
5	$8x(4x^4 - 20x^2 + 15)$
6	$8(8x^6 - 60x^4 + 90x^2 - 15)$
7	$16x(8x^6 - 84x^4 + 210x^2 - 105)$
8	$16(16x^8 - 224x^6 + 840x^4 - 840x^2 + 105)$
9	$32x(16x^8 - 288x^6 + 1512x^4 - 2520x^2 + 945)$
10	$32(32x^{10} - 720x^8 + 5040x^6 - 12600x^4 + 9450x^2 - 945)$

Table 1.2 Several associated Legendre functions

l	m	$P_l^m(x)$
1	1	$\sqrt{1-x^2}$
2	2	$3(1-x^2)$
3	2	$15x(1-x^2)$
5	2	$\dfrac{105x(1-x^2)(3x^2-1)}{2}$
7	2	$\dfrac{63x(1-x^2)(143x^4-110x^2+15)}{8}$
10	2	$\dfrac{495(1-x^2)(4199x^8-6188x^6+2730x^4-364x^2+7)}{128}$

(f) On the basis of Descartes' rule of signs what can be said about the number of positive zeros of the polynomials?

(g) Determine the exact zeros of the polynomials H_n for $n=1,2,3,4,5$.

(h) Determine the approximate zeros of the polynomials not mentioned in paragraph 1g by mathematical/spreadsheet software.

2. The associated Legendre functions $P_l^m(x)$ [2, p. 192, 4] appear in the angular parts of the orbital functions of hydrogenic (one-electron) atomic particles [3, p. 334]. Some associated Legendre functions are included in Table 1.2, and each question in this problem concerns these functions. (In each case take the longest interval of definition that is possible.)
   (a) Which functions are even and which are odd?
   (b) Which are the functions whose zeros include 0?
   (c) Which are the functions whose real zeros are symmetrical to the origin?
   (d) Which functions can have an even number of real zeros? Why?
   (e) On the basis of Descartes' rule of signs what can be said about the number of positive zeros of the polynomials?
   (f) Determine the exact zeros of the functions P_1^1, P_2^2, P_3^2, P_5^2 and P_7^2.
   (g) Determine the approximate zeros of the functions not mentioned in paragraph 2f by mathematical/spreadsheet software.

3. The associated Laguerre polynomials $L_n^k(x)$ [2, p. 76, 5] appear in the radial part of the orbital functions of hydrogenic (one-electron) atomic particles [3, p. 349]. Some of these polynomials have been collected in Table 1.3, and each question in this problem concerns these polynomials. (In each case take the longest interval of definition that is possible.)
   (a) On the basis of Descartes' rule of signs shows that the polynomials in Table 1.3 have no negative roots. What does Descartes' rule of signs say about the number of the positive roots?

Table 1.3 Several associated Laguerre polynomials

n	k	$L_n^k(x)$
1	1	$2 - x$
2	1	$\frac{x^2 - 6x + 6}{2}$
3	1	$-\frac{x^3 - 12x^2 + 36x - 24}{6}$
4	1	$\frac{x^4 - 20x^3 + 120x^2 - 240x + 120}{24}$
5	1	$-\frac{x^5 - 30x^4 + 300x^3 - 1200x^2 + 1800x - 720}{120}$

(b) Determine the exact zeros of L_1^1 and L_2^1.

(c) Determine the approximate zeros of the polynomials not mentioned in paragraph 3b by mathematical/spreadsheet software.

4. The weak acid HA partly dissociates in its aqueous solution, so the solution will also contain H^+ and A^- ions beyond the non-dissociated molecules. If we take into account the H^+ and OH^- ions originating from the dissociation of water, the concentration of the H^+ ions, $[H^+]$, in a dilute solution of the acid can be given by the equation

$$\left\{\frac{[H^+]}{c^\ominus}\right\}^3 + K_a\left\{\frac{[H^+]}{c^\ominus}\right\}^2 - \left(K_a\frac{c}{c^\ominus} + K_w\right)\left\{\frac{[H^+]}{c^\ominus}\right\} - K_aK_w = 0, \quad (1.1)$$

where $c > 0$ is the concentration of the solution, $K_a > 0$ and $K_w > 0$ are constants characterizing the dissociations of the weak acid and water, respectively, finally $c^\ominus$ is the unit of concentration.

(a) By the aid of Descartes' rule of signs show that the equation above (in accordance with the chemical meaning of the problem) has exactly one positive root.

(b) Calculate an approximate value of the positive root in paragraph 4a by mathematical/spreadsheet software if $c = 10^{-5}\,\mathrm{mol\,dm^{-3}}$ and $K_a = 5 \times 10^{-5}$.

5. In the predator–prey communities (e.g. rabbits and foxes, lions and gazelles, etc.) often both the numbers of predators and preys change periodically in time. The phases of these periodic changes are shifted: when there are many predators, there are only a few preys and vice versa. After the first investigators of this phenomenon (Volterra [6] and Lotka [7]) we assume that the prey X is reproduced proportionally to its own concentration ($v_1 = k_1[X]$), the reproduction rate of the predator Y is proportional to its own concentration and that of the

prey ($v_2 = k_2[\mathrm{X}][\mathrm{Y}]$), finally the predator perishes with a velocity proportional to the predator's concentration ($v_3 = k_3[\mathrm{Y}]$). Give the values of the concentrations [X] and [Y] for which the system is in a time-independent (stationary) state, that is $v_1 - v_2 = 0$ and $v_2 - v_3 = 0$ are simultaneously satisfied.

6. In an other version [8] of the predator–prey coexistence outlined in problem 5 the reproduction rate of the prey X is considered constant, $v_1 = k_1'$, the other interactions are the same. Calculate again the concentrations [X] and [Y] that make the system time-independent (cf. problem 5).
7. Assume that in the reaction system

$$\begin{aligned} &\mathrm{A} + 2\mathrm{X} \rightarrow 3\mathrm{X}; \qquad && v_1 = k_1'[\mathrm{A}][\mathrm{X}]^2, \\ &\mathrm{X} + 2\mathrm{Y} \rightarrow 3\mathrm{Y}; && v_2 = k_2[\mathrm{X}][\mathrm{Y}]^2, \\ &\mathrm{Y} \rightarrow \mathrm{P}; && v_3 = k_3[\mathrm{Y}], \end{aligned}$$

the amount of the substance A and that of substance P are held at constant values by appropriate matter flows. Calculate the concentrations [X] and [Y] that balance the reaction rates and make the system time-independent, that is, satisfy the equations $v_1 - v_2 = 0$ and $v_2 - v_3 = 0$.
8. Ru-Sheng Li and Hong-Jun Li [9] have investigated theoretically the behaviour of the reactions

$$\begin{aligned} &\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D} \\ &\mathrm{B} + \mathrm{C} \rightarrow 2\mathrm{B} \end{aligned}$$

in a flow reactor: the reactants A and B were continuously introduced to the reaction mixture and the volume of the latter was held at a constant value by an appropriate outflow. In this system the dimensionless concentrations of the substances A and B (x and y) vary in time according to the differential equations

$$\begin{aligned} \frac{\mathrm{d}x}{\mathrm{d}t} &= -xy + f(1-x), \\ \frac{\mathrm{d}y}{\mathrm{d}t} &= -xy + k_2 y\left[\left(1 - \frac{f_2}{f}\right)y_0 - y\right] + (f - f_2)y_0 - fy, \end{aligned}$$

where $f > 0, f_2 > 0$, $k_2 > 0$ and $y_0 > 0$ are constants. In the time-independent (stationary) state of the reactor the quantities on the left-hand sides are zeros, so the stationary values of x and y can be determined from the equations

$$\begin{aligned} -x_\mathrm{s}y_\mathrm{s} + f(1-x_\mathrm{s}) &= 0 \\ -x_\mathrm{s}y_\mathrm{s} + k_2 y_\mathrm{s}\left[\left(1 - \tfrac{f_2}{f}\right)y_0 - y_\mathrm{s}\right] + (f - f_2)y_0 - fy_\mathrm{s} &= 0. \end{aligned} \tag{1.2}$$

For simplicity we take $k_2 = 1$.

(a) Derive an one-variable equation from which the values of x_s can be determined. What is the degree of the obtained polynomial?

(b) Let $f_2 = \frac{1}{135}$ and $y_0 = \frac{10}{27}$. Select f values from the interval $-1.7 \leq \log f \leq -1.2$, and solve the equation obtained in paragraph 8a with these. Plot the root(s) x_s against $\log f$. Are there any f values for which this equation has more than one positive root? What word would you associate with the diagram obtained?

(c) Let $f_2 = 0.001$ and $y_0 = 0.25$. Select f values from the interval $-3 \leq \log f \leq -1$, and solve the equation obtained in paragraph 8a with these. Plot the root(s) x_s against $\log f$. Are there any f values for which this equation has more than one positive root? Why can we associate the word "isola" with the diagram obtained?

(d) Perform the tasks in paragraph 8c for $f_2 = 0.001$, $y_0 = 0.29$ and $-3 \leq \log f \leq -1$. What word would you associate with the diagram obtained?

Use mathematical/spreadsheet software for the calculations.

9. Turcsányi and Kelen [10] have investigated an oscillatory reaction model based on "catastrophic changes of state". To determine the time-independent (stationary) state of the reaction system

$$\mathrm{X} \rightleftharpoons \mathrm{Y}, \quad \mathrm{X} \rightleftharpoons \mathrm{Z}, \quad \mathrm{X} \rightleftharpoons \mathrm{W},$$
$$\mathrm{Y} + \mathrm{Z} \rightarrow 2\mathrm{Y}, \quad \mathrm{Y} + \mathrm{W} \rightarrow 2\mathrm{X}$$

they solved the system of equations

$$\begin{aligned}
-k_1x_\mathrm{s} + k_2y_\mathrm{s} - k_3x_\mathrm{s} + k_4z_\mathrm{s} - k_5x_\mathrm{s} + k_6w_\mathrm{s} + 2k_8y_\mathrm{s}w_\mathrm{s} &= 0\\
k_1x_\mathrm{s} - k_2y_\mathrm{s} + k_7y_\mathrm{s}z_\mathrm{s} - k_8y_\mathrm{s}w_\mathrm{s} &= 0\\
k_3x_\mathrm{s} - k_4z_\mathrm{s} - k_7y_\mathrm{s}z_\mathrm{s} &= 0\\
k_5x_\mathrm{s} - k_6w_\mathrm{s} - k_8y_\mathrm{s}w_\mathrm{s} &= 0
\end{aligned}$$

in which $x_\mathrm{s}, y_\mathrm{s}, z_\mathrm{s}$ and w_s denote the unknown stationary concentrations of the corresponding substances and $k_1, k_2, \ldots, k_8$ the given (positive) rate coefficients.

(a) How many solutions $(x_\mathrm{s}, y_\mathrm{s}, z_\mathrm{s}, w_\mathrm{s})$ does the system of equations above have?

(b) Let

$$b = x_\mathrm{s} + y_\mathrm{s} + z_\mathrm{s} + w_\mathrm{s}.$$

To calculate y_s derive an equation of the form

$$f(y_s, b, k_1, \ldots, k_8) = 0. \tag{1.3}$$

(c) In appropriate units let $k_1 = 1.8$, $k_2 = 1$, $k_3 = 8$, $k_4 = 8$, $k_5 = 5$, $k_6 = 3$, $k_7 = 8$ and $k_8 = 20$. Plot the roots of Eqn (1.3) against b in the interval $1.5 \leq b \leq 3$. Are there any b values for which Eqn (1.3) has more than one positive root?

Use mathematical/spreadsheet software for the calculations.

10. Gray and Scott [11] have studied the reactions

$$\mathrm{A} + 2\mathrm{B} \rightarrow 3\mathrm{B},$$
$$\mathrm{B} \rightarrow \mathrm{C}$$

in an isothermal reactor that was open to matter flow. The differential equation system describing the time evolution of the reactor is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = -\alpha\beta^2 + \frac{1-\alpha}{\tau_{\mathrm{res}}},$$
$$\frac{\mathrm{d}\beta}{\mathrm{d}\tau} = \alpha\beta^2 - \frac{\beta}{\tau_2} - \frac{\beta - \beta_0}{\tau_{\mathrm{res}}},$$

where $\alpha \geq 0$ and $\beta \geq 0$ are the dimensionless concentrations of the substances A and B, respectively, and $\beta_0 \geq 0$, $\tau_{\mathrm{res}} > 0$ and $\tau_2 > 0$ the parameters. In the time-independent (stationary) state of the system the quantities on the left-hand sides are zeros, so we have

$$-\alpha_s\beta_s^2 + \frac{1-\alpha_s}{\tau_{\mathrm{res}}} = 0,$$
$$\alpha_s\beta_s^2 - \frac{\beta_s}{\tau_2} - \frac{\beta_s - \beta_0}{\tau_{\mathrm{res}}} = 0 \tag{1.4}$$

for the stationary concentrations α_s and β_s.

(a) Derive an one-variable equation from which α_s can be determined. What is the degree of the equation found? On the basis of Descartes' rule of signs how many positive roots can this equation have?

(b) In the case of $\beta_0 = 0$ the one-variable equation found in paragraph 10a can be solved analytically [11].

  i. Factorize this equation and determine its roots as functions of the parameter τ_{res}. Show that in the case of $\tau_2 > 16$ there exist $0 < p < q$ such that the equation has three distinct positive roots if $p < \tau_{\mathrm{res}} < q$.

   ii. For $\tau_2 = 20$ plot α_s against τ_{res} in the interval where three distinct roots occur. Compare the figure obtained with Fig. 2.2.

11. In a kinetic system containing two intermediates and at most second-order reactions the time-independent (stationary) state of the system is described by the equations

$$\begin{aligned} P(x_s, y_s) &= k_0 + k_1 x_s + k_2 y_s + k_3 x_s^2 + k_4 x_s y_s + k_5 y_s^2 = 0, \\ Q(x_s, y_s) &= c_0 + c_1 y_s + c_2 x_s + c_3 y_s^2 + c_4 y_s x_s + c_5 x_s^2 = 0, \end{aligned} \tag{1.5}$$

where x_s and y_s stand for the unknown stationary concentrations of the intermediates X and Y, respectively. For the constants on the right-hand sides it is known that

$$k_0, k_2, k_5, c_0, c_2, c_5 \geq 0$$

and

$$k_3, c_3 \leq 0.$$

The behaviour of the system diverted from its stationary state greatly depends [12, 13, 14, p. 697] on the solutions of the quadratic equation

$$\lambda^2 - \mathrm{Tr}\lambda + \Delta = 0 \tag{1.6}$$

where

$$\mathrm{Tr} = \partial_1 P(x_s, y_s) + \partial_2 Q(x_s, y_s),$$

$$\Delta = \partial_1 P(x_s, y_s) \partial_2 Q(x_s, y_s) - \partial_2 P(x_s, y_s) \partial_1 Q(x_s, y_s),$$

$$\partial_1 P(x_s, y_s) = k_1 + 2k_3 x_s + k_4 y_s,$$

$$\partial_1 Q(x_s, y_s) = c_2 + c_4 y_s + 2c_5 x_s,$$

$$\partial_2 P(x_s, y_s) = k_2 + k_4 x_s + 2k_5 y_s$$

and

$$\partial_2 Q(x_s, y_s) = c_1 + 2c_3 y_s + c_4 x_s.$$

Let λ_1 and λ_2 be the roots of Eqn (1.6) calculated with a positive solution (x_s, y_s) of Eqn (1.5). Using the quadratic formula

(a) determine the signs of λ_1 and λ_2 when they are real, non-zero and have the same sign [12, 13];

(b) determine the signs of the real parts of λ_1 and λ_2 when they are complex but not purely imaginary [12, 13];

(c) show [12, 13] that for purely imaginary λ_1 and λ_2 Eqn (1.5) has the form

$$\begin{aligned} P(x_s, y_s) &= k_1 x_s + k_4 x_s y_s = 0, \\ Q(x_s, y_s) &= c_1 y_s + c_4 y_s x_s = 0. \end{aligned}$$

12. The Oregonator model of the oscillating Belousov–Zhabotinsky reaction [15] consists of the following reaction steps:

$$\begin{aligned} &\mathrm{A} + \mathrm{Y} \to \mathrm{X}, \\ &\mathrm{X} + \mathrm{Y} \to \mathrm{P}, \\ &\mathrm{B} + \mathrm{X} \to 2\mathrm{X} + \mathrm{Z}, \\ &2\mathrm{X} \to \mathrm{Q}, \\ &\mathrm{Z} \to f\mathrm{Y}, \end{aligned}$$

where $\mathrm{X} = \mathrm{HBrO_2}$, $\mathrm{Y} = \mathrm{Br^-}$, $\mathrm{Z} = 2\mathrm{Ce(IV)}$, $\mathrm{A} = \mathrm{B} = \mathrm{BrO_3^-}$ and $f > 0$ is an adjustable parameter. The concentrations of X, Y and Z in the time-independent (stationary) state of the system, x_s, y_s, z_s, are determined by the system of equations

$$\begin{aligned} y_s - x_s y_s + x_s - q x_s^2 &= 0, \\ f z_s - y_s - x_s y_s &= 0, \\ x_s - z_s &= 0, \end{aligned} \tag{1.7}$$

where $q > 0$ is a constant. Hsü [16] investigated this system in detail in order to prove that the kinetic equations of the Oregonator model can have a positive periodic solution. Following Hsü's work solve the following problems:

(a) Determine the solution (x_s, y_s, y_s) of Eqn (1.7).

(b) The stability of the solution (x_s, y_s, y_s) is determined by the roots of the equation

$$\lambda^3 + A(w)\lambda^2 + B(w)\lambda + C(w) = 0, \tag{1.8}$$

where $w > 0$ is a variable parameter,

$$A(w) = w + \alpha,$$

$$B(w) = \left[2qx_s^2 + x_s(q-1) + f\right] + \alpha w,$$

$$C(w) = w x_s[2q x_s + (q-1) + f],$$

$$\alpha = r y_s + \left(\frac{1}{r} + 2qr\right) x_s + \frac{1}{r} - r,$$

Table 1.4 Several spherical Bessel functions of the first kind (j_n)

n	$j_n(x)$
0	$\dfrac{\sin x}{x}$
1	$\dfrac{\sin x}{x^2} - \dfrac{\cos x}{x}$
2	$\left(\dfrac{3}{x^3} - \dfrac{1}{x}\right)\sin x - \dfrac{3}{x^2}\cos x$
3	$\dfrac{(x^2-15)\cos x}{x^3} + \dfrac{3(5-2x^2)\sin x}{x^4}$

and $r > 0$ is a constant. Let now (x_s, y_s, y_s) be the positive solution of Eqn (1.7).

i. Show that $A(w)$, $C(w)$ and α are all positive.
ii. Suppose that $2qx_s^2 + x_s(q-1) + f < 0$ and show that there is a unique $w_s > 0$ at which the equation $\lambda^3 + A(w_s)\lambda^2 + B(w_s)\lambda + C(w_s) = 0$ has two imaginary roots and a real one.

13. In the quantum mechanical description of the particle in a sphere the solutions contain spherical Bessel functions [17, 18, p. 437]. The first few of these functions are collected in Table 1.4. Some preliminary considerations suggest that the function j_0 has four roots in the interval (0, 14) and the other functions in the table have three roots. Determine these roots. Use mathematical/spreadsheet software.
14. If we direct a beam of appropriately accelerated electrons to a sample of CO_2 gas at low pressure, we can determine the distances of the atoms in the CO_2 molecule (electron diffraction, [3, p. 642]). The intensity of the electron beam scattered on the gas molecules is given by the expression

$$I(x) = N\left[2\cdot 8\cdot 8 + 6\cdot 6 + 4\cdot 8\cdot 6\frac{\sin x}{x} + 2\cdot 8\cdot 8\frac{\sin 2x}{2x}\right],$$

where N is a constant and x a dimensionless parameter, which is proportional to the angle between the directions of the incident and the diverted electron beams. The integers 6 and 8 are the atomic numbers of carbon and oxygen, respectively. The local maxima and minima of the function I can be determined from the roots of the equation

$$\frac{3\cos x}{x} - \frac{3\sin x}{x^2} + \frac{2\cos 2x}{x} - \frac{\sin 2x}{x^2} = 0 \qquad (1.9)$$

obtained by the differentiation of I. According to some preliminary considerations Eqn (1.9) has eight roots in the interval $(5, 30)$. Determine these roots by a numerical procedure. Use mathematical/spreadsheet software.

15. The equilibrium constant of the reaction $CO + 2H_2 \rightleftharpoons CH_3OH$ is $K_x = 2.1$ at 400 K and 1 bar. If the initial reaction mixture contains $n(CO)$ and $n(H_2)$ moles of the reactants, and the proportion of CO depleted until the equilibrium is reached is x then

$$K_x = \frac{a^2 x n(\mathrm{CO})}{(1-x)n(\mathrm{CO})[n(\mathrm{H_2}) - 2xn(\mathrm{CO})]^2}, \tag{1.10}$$

where

$$a = (1-2x)n(\mathrm{CO}) + n(\mathrm{H_2}).$$

   (a) Transform Eqn (1.10) into an equation of the form $f(x) = 0$ where f is a polynomial. On the basis of Descartes' rule of signs how many positive roots does this equation have? (Assume that all the coefficients are different from zero.)

   (b) We are interested in the roots of the equation obtained in paragraph 15a that lie in the interval $[0, 1]$. Calculate these roots for the following cases:
      i. $n(CO) = 1$ mol and $n(H_2) = 1$ mol;
      ii. $n(CO) = 1$ mol and $n(H_2) = 2$ mol (stoichiometric ratio);
      iii. $n(CO) = 3$ mol and $n(H_2) = 1$ mol.

   Which of these roots satisfy Eqn (1.10) as well? Which roots are chemically meaningful? Which case produces the maximal x value? Can you formulate a conjecture on the basis of these calculations? (Hint: in paragraph 15(b)i show that 1 is a root of the equation to be solved and give the equation as the product of a linear factor and a quadratic one; in the other paragraphs use mathematical/spreadsheet software.)

16. The equilibrium constant of the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is $K_x = 44.7$ at 400 K and 1 bar. If the initial mixture contains $n(N_2)$ and $n(H_2)$ moles of the reactants, and the proportion of N_2 depleted until the equilibrium is reached is x then

$$K_x = \frac{4x^2 a^2 n(\mathrm{N_2})^2}{(1-x)n(\mathrm{N_2})[n(\mathrm{H_2}) - 3xn(\mathrm{N_2})]^3}, \tag{1.11}$$

where

$$a = (1-2x)n(\mathrm{N_2}) + n(\mathrm{H_2}).$$

   (a) Transform Eqn (1.11) into an equation of the form $f(x) = 0$ where f is a polynomial. On the basis of Descartes' rule of signs how many positive roots does this equation have? (Assume that all the coefficients are different from zero.)

(b) We are interested in the roots of the equation obtained in paragraph 16a that lie in the interval [0, 1]. Calculate these roots for the following cases:
   i. $n(\mathrm{N_2}) = 1$ and $n(\mathrm{H_2}) = 1$;
   ii. $n(\mathrm{N_2}) = 1$ and $n(\mathrm{H_2}) = 3$ (stoichiometric ratio);
   iii. $n(\mathrm{N_2}) = 3$ and $n(\mathrm{H_2}) = 1$.

Which of these roots satisfy Eqn (1.11) as well? Which roots are chemically meaningful? Which case produces the maximal x value? Can you formulate a conjecture on the basis of these calculations? (Hint: in paragraph 16(b)i show that 1 is a root of the equation to be solved, and give the corresponding polynomial as the product of a linear factor and a cubic one; in paragraph 16(b)ii give the polynomial investigated as the product of two quadratic factors; use mathematical/spreadsheet software for the solutions of the cubic and quadratic equations.)

17. The Redlich–Kwong equation of state for the real gases is

$$p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{T^{1/2}} \cdot \frac{1}{V_\mathrm{m}(V_\mathrm{m} + b)}.$$

Epstein [19] determined exactly how the constants $a > 0$ and $b > 0$ are related to the pressure ($p_\mathrm{c} > 0$), molar volume ($V_\mathrm{mc} > 0$) and temperature ($T_\mathrm{c} > 0$) of the given gas at its critical point. We shall follow his considerations.

(a) Divide the formula

$$\frac{RT_\mathrm{c}^{3/2}}{(V_\mathrm{mc} - b)^2} = a\frac{2V_\mathrm{mc} + b}{(V_\mathrm{mc}^2 + bV_\mathrm{mc})^2} \tag{1.12}$$

by

$$\frac{RT_\mathrm{c}^{3/2}}{(V_\mathrm{mc} - b)^3} = a\frac{3V_\mathrm{mc}^2 + 3bV_\mathrm{mc} + b^2}{(V_\mathrm{mc}^2 + bV_\mathrm{mc})^3} \tag{1.13}$$

and introduce

$$V_\mathrm{mc} = xb \tag{1.14}$$

($x > 0$) into the result. Give the cubic equation that determines x. (Both Eqns (1.12) and (1.13) originate from the formula

$$\frac{\partial p}{\partial V_\mathrm{m}}(V_\mathrm{mc}, T_\mathrm{c}) = \frac{\partial^2 p}{\partial V_\mathrm{m}^2}(V_\mathrm{mc}, T_\mathrm{c}) = 0).$$

(b) Show that the equation obtained in paragraph 17a has only one positive root, and calculate the exact value of this root.

(c) Using the formulas above and

$$p_{\mathrm{c}} = \frac{RT_{\mathrm{c}}}{V_{\mathrm{mc}} - b} - \frac{a}{T_{\mathrm{c}}^{1/2}} \cdot \frac{1}{V_{\mathrm{mc}}(V_{\mathrm{mc}} + b)} \tag{1.15}$$

show that

$$T_{\mathrm{c}} = \left(\frac{3a}{bRx^2} \right)^{2/3}$$

moreover,

$$p_{\mathrm{c}} = \left(\frac{a^2 R}{3b^5 x^7} \right)^{1/3}.$$

(d) Utilizing the formulas obtained so far determine the numerical value of the compressibility factor

$$Z_{\mathrm{c}} = \frac{p_{\mathrm{c}} V_{\mathrm{mc}}}{RT_{\mathrm{c}}}.$$

18. Using the van der Waals equation [3, p. 33],

$$\left(p + \frac{n^2 a}{V^2} \right)(V - nb) = nRT,$$

calculate the volume of 1 mol of N_2 gas at $p = 10^6$ Pa and $T = 298$ K ($a = 0.1427\,\mathrm{m^6\,Pa\,mol^{-2}}$, $b = 3.913 \times 10^{-5}\,\mathrm{m^3 mol^{-1}}$):

(a) Derive the cubic equation that determines the volume V.

(b) Substitute the numerical data into the cubic equation obtained, and give the number of the positive roots by the aid of Descartes' rule of signs.

(c) Solve the cubic equation by mathematical/spreadsheet software. If necessary, obtain an initial volume value from the perfect gas law

$$pV = nRT.$$

19. The enthalpy of vaporization of the various liquids may depend on temperature. For the isobutane this dependence is given by the formula

$$\frac{\Delta H(\mathrm{kJ\,mol^{-1}})}{T/\mathrm{K}} = 0.841 - 0.314\,\log(T/\mathrm{K})$$

in the 240–400 K temperature range [20, p. 190]. Determine the temperature T at which the enthalpy of vaporization of isobutane is $\Delta H = 18\,\mathrm{kJ\,mol^{-1}}$. Use mathematical/spreadsheet software. (Hint: the equation obtained with the substitution $\Delta H = 18\,\mathrm{kJ\,mol^{-1}}$ has one positive root in the range 240–400 K.)

20. Assuming full dissociation calculate the solubilities of the sparingly soluble salts AgCl and AgI in a $b = 10^{-4}\,\mathrm{mol\,kg^{-1}}$ KNO_3 solution at 25°C. The solubility constants of the salts are [21, p. 615]: $L_a(\mathrm{AgCl}) = 1.0 \times 10^{-10}$ and $L_a(\mathrm{AgI}) = 1.0 \times 10^{-16}$. For a salt with the general formula $\mathrm{M}^{|z_\mathrm{M}|+}\mathrm{A}^{|z_\mathrm{A}|-}$ that is dissolved in a solution of the electrolyte $\mathrm{X}^{|z_\mathrm{X}|+}\mathrm{Y}^{|z_\mathrm{Y}|-}$, the equation to be solved (cf. [22, p. 336, 364]) is

$$L_a = \left(\frac{S}{b^{\ominus}}\right)^2 10^{-2A|z_\mathrm{M} z_\mathrm{A}|\sqrt{\frac{1}{2}\left(S z_\mathrm{M}^2 + S z_\mathrm{A}^2 + b z_\mathrm{X}^2 + b z_\mathrm{Y}^2\right)}}, \tag{1.16}$$

where S is the unknown solubility, b the molality (molal concentration) of the electrolyte solution, $b^{\ominus}$ the unit of molality and $A = 0.509\ (\mathrm{mol\,kg^{-1}})^{-1/2}$. In our case evidently $z_\mathrm{X} = -z_\mathrm{Y} = z_\mathrm{M} = -z_\mathrm{A} = 1$. In the usual solution of this equation – utilizing the small solubility of the salt – we assume that $S \ll b$ and substitute $S = 0$ in the expression under the radical sign. Thus, we obtain S from a quadratic equation.

(a) Solve Eqn (1.16) with the simplification above for the cases of AgCl and AgI.

(b) In order to confirm the results obtained in the previous paragraph solve Eqn (1.16) without any simplification for the cases of AgCl and AgI. Are there roots in the vicinities of those obtained in the previous paragraph? Are there other roots as well? Use approximate methods and mathematical/spreadsheet software.

21. In the LCAO–MO (Linear Combination of Atomic Orbitals–Molecular Orbital) description of the H_2^+ ion the equilibrium distance R_AB between the H nuclei A and B can be calculated from the following equation (after [3, pp. 397, 398], [23, p. 223]):

$$\begin{aligned} &3e^{2d}(2d^3 - 2d^2 - 3d - 3) + e^d(2d^4 - 33d^2 - 36d - 18) \\ &\quad -3(d^4 + 6d^3 + 12d^2 + 9d + 3) = 0, \end{aligned} \tag{1.17}$$

where $d = R_\mathrm{AB}/a_0$ and a_0 the Bohr radius. What is the value of the equilibrium bond distance R_AB in the H_2^+ ion according to the applied LCAO–MO approximation? Use mathematical/spreadsheet software for the calculations. (Hint: the root that we need is in the interval $(2, 3)$, and is unique there.)

1.2 LINEAR ALGEBRA

1. A chemical reaction equation must express that the electric charge and the atomic species are conserved in chemical processes. The conservation equations (one for each atomic species and an extra one for the electric charge) form a linear system of equations whose unknowns are the stoichiometric coefficients of the reaction equation. Construct this system of equations and determine the stoichiometric coefficients for each of the reactions below. Each case gives how many stoichiometric coefficients can be chosen arbitrarily.
   (a) $x\mathrm{H_2} + y\mathrm{O_2} = z\mathrm{H_2O}$
   (b) $x\mathrm{Ca(OH)_2} + y\mathrm{S_2} = z\mathrm{CaS_5} + u\mathrm{CaS_2O_3} + v\mathrm{H_2O}$
   (c) $x\mathrm{S} + y\mathrm{O_2} + z\mathrm{H_2O} = u\mathrm{H_2SO_4}$
   (d) $x\mathrm{HCl} + y\mathrm{MnO_2} = z\mathrm{MnCl_2} + u\mathrm{H_2O} + v\mathrm{Cl_2}$
   (e) $x\mathrm{KMnO_4} + y\mathrm{HCl} = z\mathrm{KCl} + u\mathrm{MnCl_2} + v\mathrm{H_2O} + w\mathrm{Cl_2}$
   (f) $x\mathrm{K_2Cr_2O_7} + y\mathrm{HCl} = z\mathrm{KCl} + u\mathrm{CrCl_3} + v\mathrm{H_2O} + w\mathrm{Cl_2}$
   (g) $x\mathrm{Br^-} + y\mathrm{MnO_2} + z\mathrm{H^+} = u\mathrm{Br_2} + v\mathrm{Mn^{2+}} + w\mathrm{H_2O}$
   (h) $x\mathrm{Br^-} + y\mathrm{Cl_2} = z\mathrm{Cl^-} + u\mathrm{Br_2}$
   (i) $x\mathrm{IO_3^-} + y\mathrm{I^-} + z\mathrm{H^+} = u\mathrm{I_2} + v\mathrm{H_2O}$
   (j) $x\mathrm{KMnO_4} + y\mathrm{H_2SO_4} + z\mathrm{H_2O_2} = u\mathrm{MnSO_4} + v\mathrm{K_2SO_4} + w\mathrm{H_2O} + r\mathrm{O_2}$
2. The stoichiometric matrix, which briefly describes the given reaction system, is introduced in Appendix A. The rank of this matrix gives the number of the linearly independent reactions in the reaction system. Using the given numbering construct this matrix for the following reaction systems:
   (a) formation of hydrogen peroxide,

$$\mathrm{H_2}(1) + \mathrm{O_2}(2) = \mathrm{H_2O_2}(3)\ [1]$$

   (b) dissociation of carbonic acid,

$$\begin{aligned} \mathrm{H_2CO_3}(1) &= \mathrm{HCO_3^-}(2) + \mathrm{H^+}(3)\ [1] \\ \mathrm{HCO_3^-} &= \mathrm{CO_3^{2-}}(4) + \mathrm{H^+} \qquad [2] \end{aligned}$$

   (c) Ogg's mechanism for the decomposition of nitrogen pentoxide [24, p. 303],

$$\begin{aligned} \mathrm{N_2O_5}(1) &= \mathrm{NO_2}(2) + \mathrm{NO_3}(3) && [1] \\ \mathrm{NO_2} + \mathrm{NO_3} &= \mathrm{N_2O_5} && [2] \\ \mathrm{NO_2} + \mathrm{NO_3} &= \mathrm{NO_2} + \mathrm{O_2}(4) + \mathrm{NO}(5) && [3] \\ \mathrm{NO} + \mathrm{N_2O_5} &= 3\mathrm{NO_2} && [4] \end{aligned}$$

(d) the mechanism proposed by Christiansen, Herzfeld and Polanyi for the thermal hydrogen–bromine reaction [24, p. 291],

$$\begin{array}{rcll}
\mathrm{Br_2}(1) &=& \mathrm{2Br}(2) & [1]\\
\mathrm{Br} + \mathrm{H_2}(3) &=& \mathrm{HBr}(4) + \mathrm{H}(5) & [2]\\
\mathrm{H} + \mathrm{Br_2} &=& \mathrm{HBr} + \mathrm{Br} & [3]\\
\mathrm{H} + \mathrm{HBr} &=& \mathrm{H_2} + \mathrm{Br} & [4]\\
\mathrm{Br} + \mathrm{Br} &=& \mathrm{Br_2} & [5]
\end{array}$$

(e) a mechanism suggested by Bodenstein and Plaut for the formation and decomposition of phosgene [24, p. 302],

$$\begin{array}{rcll}
\mathrm{Cl_2}(1) &=& \mathrm{2Cl}(2) & [1]\\
\mathrm{2Cl} &=& \mathrm{Cl_2} & [2]\\
\mathrm{Cl} + \mathrm{CO}(3) &=& \mathrm{COCl}(4) & [3]\\
\mathrm{COCl} &=& \mathrm{Cl} + \mathrm{CO} & [4]\\
\mathrm{COCl} + \mathrm{Cl_2} &=& \mathrm{COCl_2}(5) + \mathrm{Cl} & [5]\\
\mathrm{COCl_2} + \mathrm{Cl} &=& \mathrm{COCl} + \mathrm{Cl_2} & [6]
\end{array}$$

(f) Michaelis–Menten mechanism of enzyme catalysis [24, p. 400]:

$$\begin{array}{rcll}
\mathrm{E}(1) + \mathrm{S}(2) &=& \mathrm{ES}(3) & [1]\\
\mathrm{ES} &=& \mathrm{E} + \mathrm{S} & [2]\\
\mathrm{ES} &=& \mathrm{P}(4) + \mathrm{E} & [3]
\end{array}$$

(g) Lotka–Volterra model [6, 7],

$$\begin{array}{rcll}
\mathrm{A}(1) + \mathrm{X}(2) &=& \mathrm{2X} & [1]\\
\mathrm{X} + \mathrm{Y}(3) &=& \mathrm{2Y} & [2]\\
\mathrm{Y} &=& \mathrm{P}(4) & [3]
\end{array}$$

Determine the rank of the stoichiometric matrix in each case.

3. Suppose that in a reaction system there is a new species in each of the subsequent reactions. What is the relationship between the rank of the stoichiometric matrix (see Appendix A) and the number of the reactions? Why?
4. The formula matrix is defined in Appendix A. Construct the formula matrices for the systems (a)–(e) in problem 2. Moreover, construct the formula matrices for the following systems that are given by their constituents:
   (a) $\mathrm{CaC_2O_4}, \mathrm{Ca^{2+}}, \mathrm{C_2O_4^{2-}}, \mathrm{HC_2O_4^{-}}, \mathrm{H_2C_2O_4}, \mathrm{H^+}$
   (b) $\mathrm{Na_3PO_4}, \mathrm{Na_2HPO_4}, \mathrm{NaH_2PO_4}, \mathrm{H_3PO_4}, \mathrm{NaOH}, \mathrm{H_2O}$

(c) H_2, CO, O_2, H_2O, CO_2
(d) $CH_4, H_2O, CO, CO_2, H_2, CH_3OH, O_2$
Determine the rank of the formula matrix in each case.

5. Determine the maximal number of the linearly independent reactions for the chemical systems given in problem 4, and give two sets of linearly independent reactions in each case where this is possible. (Hint: use the material in Appendix A. For the construction of linearly independent solutions of linear systems of equations see, for example, [25, p. 92] and in a stoichiometric context [26].)
6. Gutman et al. [27] and Fishtik et al. [28] while investigating theoretically how the equilibria of the chemical systems shift as a result of external factors, introduced the notion of the "Hessian response reaction": In a system that contains R reactions ($R > 1$) and N substances any linear combination of the original reactions that involves at most $N-(R-1)$ substances is called a Hessian response reaction. Let us write the reactions in the system into the form

$$\sum_{i=1}^{N} \nu_{ij}\mathrm{B}_i = 0 \quad j = 1, 2, \ldots, R$$

where $\mathrm{B}_1, \mathrm{B}_2, \ldots, \mathrm{B}_N$ are the substances and ν_{ij} is the stoichiometric coefficient of the ith substance in the jth reaction. The general form of the linear combinations of these reactions is

$$\sum_{j=1}^{R} c_j \left(\sum_{i=1}^{N} \nu_{ij}\mathrm{B}_i \right) = \sum_{i=1}^{N} \left(\sum_{j=1}^{R} \nu_{ij}c_j \right) \mathrm{B}_i = 0 \tag{1.18}$$

where $c_1, c_2, \ldots c_R$ are arbitrary coefficients. Define the ν_i quantities as

$$\nu_i = \sum_{j=1}^{R} \nu_{ij}c_j, \quad i = 1, 2, \ldots, N. \tag{1.19}$$

By the determination of the coefficients $c_1, c_2, \ldots, c_R$ show that if the response reaction

$$\sum_{i=1}^{N} \nu_i\mathrm{B}_i = 0$$

has been obtained from Eqn (1.18) by the elimination of the substances $B_{i_1}, B_{i_2}, \ldots, B_{i_{R-1}}$ then

$$\nu_i = c\begin{vmatrix} \nu_{i_1 1} & \nu_{i_1 2} & \cdots & \nu_{i_1 R} \\ \nu_{i_2 1} & \nu_{i_2 2} & \cdots & \nu_{i_2 R} \\ \vdots & \vdots & & \vdots \\ \nu_{i_{R-1} 1} & \nu_{i_{R-1} 2} & \cdots & \nu_{i_{R-1} R} \\ \nu_{i1} & \nu_{i2} & \cdots & \nu_{iR} \end{vmatrix}; \qquad i = 1, 2, \ldots, N,$$

where c is a coefficient that is independent of the index i [27], [28]. Assume that the rank of the matrix composed of the first $R-1$ rows of the previous determinant is $R-1$.

7. The temporal changes of the concentrations in the reversible "triangle reaction"

$$\begin{aligned} B_1 &\rightleftharpoons B_2, \\ B_2 &\rightleftharpoons B_3, \\ B_3 &\rightleftharpoons B_1, \end{aligned} \tag{1.20}$$

depend on the eigenvalues of the kinetic matrix

$$\mathbf{C} = \begin{pmatrix} -(k_1 + k_3') & k_1' & k_3 \\ k_1 & -(k_1' + k_2) & k_2' \\ k_3' & k_2 & -(k_2' + k_3) \end{pmatrix},$$

where $k_1, k_2, k_3, k_1', k_2'$ and k_3' are the positive rate coefficients. (We assume that the temperature, pressure and volume of the system are constant and there is no exchange of matter with the surroundings.) The principle of detailed balance [24, p. 130, 29] states that a reversible reaction system is balanced if and only if each component reaction is balanced. In our case this implies

$$\frac{k_1}{k_1'}\frac{k_2}{k_2'}\frac{k_3}{k_3'} = 1. \tag{1.21}$$

(a) Show that if Eqn (1.21) is valid then the eigenvalues of the matrix $\mathbf{C}$ are real. Employ the following statements:
   - The eigenvalues of the matrices $\mathbf{A}$ and $\mathbf{B}$ are the same if there exists a matrix $\mathbf{Q}$ such that $\mathbf{B} = \mathbf{QAQ}^{-1}$ [30, p. 98].
   - The eigenvalues of a real symmetric matrix are real [30, p. 100].

(b) Let $k_1 = k_1' = k_0, k_2 = k_2' = 2k_0$ and $k_3 = k_3' = 3k_0$, where $k_0 > 0$. Assuming the validity of Eqn (1.21) determine the eigenvalues of the matrix **C**.

8. When we neglect the reverse reactions in the model (1.20) we obtain the "irreversible triangle reaction"

$$\begin{aligned} &\mathrm{B}_1 \rightarrow \mathrm{B}_2, \\ &\mathrm{B}_2 \rightarrow \mathrm{B}_3, \\ &\mathrm{B}_3 \rightarrow \mathrm{B}_1. \end{aligned} \tag{1.22}$$

In this model the temporal changes of the concentrations depend on the eigenvalues of the kinetic matrix

$$\mathbf{C} = \begin{pmatrix} -k_1 & 0 & k_3 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & -k_3 \end{pmatrix}.$$

Show that there exist positive k_1, k_2 and k_3 rate coefficients for which the eigenvalues of **C** are not all real. (In this sense the behaviour of this simplified model does not correspond to that of the correct reversible model.)

9. The temporal behaviour of a first-order reaction system is characterized by the eigenvalues of the kinetic matrix. Below we present the kinetic matrices of some first-order reaction systems (assuming that the systems are closed and their temperatures, pressures and volumes are constant). The k_i rate coefficients in the kinetic matrix **C** are positive quantities. Determine the eigenvalues of the kinetic matrix in each case. For which case is it true that the eigenvalues are real non-positive quantities? How many zero eigenvalues do exist in these cases? The cases to be investigated are

(a) the $N \times N$ kinetic matrix of the consecutive first-order reaction system $B_1 \rightarrow B_2 \rightarrow \ldots \rightarrow B_N \quad (N > 2)$,

$$\mathbf{C} = \begin{pmatrix} -k_1 & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 \\ k_1 & -k_2 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 \\ 0 & k_2 & -k_3 & 0 & \ldots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \ldots & 0 & k_{N-2} & -k_{N-1} & 0 \\ 0 & 0 & 0 & 0 & \ldots & 0 & 0 & k_{N-1} & 0 \end{pmatrix};$$

(b) the $(N+1)\times(N+1)$ kinetic matrix of the parallel first-order reaction system

$$\begin{aligned}&A \rightarrow B_1,\\&A \rightarrow B_2,\\&\quad\vdots\\&A \rightarrow B_N,\end{aligned}$$

$$\mathbf{C} = \begin{pmatrix} -\sum_{i=1}^{N} k_i & 0 & \dots & 0 & 0 \\ k_1 & 0 & \dots & 0 & 0 \\ k_2 & 0 & \dots & 0 & 0 \\ \vdots & \vdots & & \vdots & \vdots \\ k_N & 0 & \dots & 0 & 0 \end{pmatrix};$$

(c) the 3×3 kinetic matrix of the first-order reaction sequence $B_1 \rightleftharpoons B_2 \rightarrow B_3$,

$$\mathbf{C} = \begin{pmatrix} -k_1 & k_1' & 0 \\ k_1 & -(k_1'+k_2) & 0 \\ 0 & k_2 & 0 \end{pmatrix}.$$

10. In a given reaction system the time-independent (stationary) concentrations of the intermediates are determined by the matrix equation

$$\begin{pmatrix} \nu_{11} & \nu_{12} & \dots & \nu_{1R} \\ \nu_{21} & \nu_{22} & \dots & \nu_{2R} \\ \vdots & \vdots & & \vdots \\ \nu_{N1} & \nu_{N2} & \dots & \nu_{NR} \end{pmatrix} \begin{pmatrix} w_1 \\ w_2 \\ \vdots \\ w_R \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \tag{1.23}$$

in which $\{\nu_{ij}\}$ is the stoichiometric matrix of the intermediates and $\{w_j\}$ the column vector of the unknown reaction rates. (The ν_{ij} element of the stoichiometric matrix gives the stoichiometric coefficient of the ith substance in the jth reaction, see Appendix A.) In one of the methods that aim to make the difficult reaction systems more transparent [31] the linearly independent solutions of Eqn (1.23) are regarded as "reaction routes" to which some "net" reaction equations are assigned. To create a "net" reaction equation we respectively multiply the R reactions in the stoichiometric matrix – which still contains the reactants and the products beyond the intermediates – by the components of one of the linearly independent solutions $(w_1\, w_2\, \dots\, w_R)^{\mathrm{T}}$, and add the obtained equations. The “net” reaction equations do not contain the intermediates any more. Following Masuda’s work [31] give the stoichiometric matrix of the intermediates (Eqn (1.23)) and a set of “reaction routes” together with the corresponding “net” reaction equations for the following systems:

(a) the Brusselator model [32],

$$\begin{aligned} \mathrm{A} &= \mathrm{X} && [1]\\ \mathrm{B}+\mathrm{X} &= \mathrm{Y}+\mathrm{D} && [2]\\ 2\mathrm{X}+\mathrm{Y} &= 3\mathrm{X} && [3]\\ \mathrm{X} &= \mathrm{E}, && [4] \end{aligned}$$

the intermediates and their numbers are X(1) and Y(2);

(b) a model of the Belousov–Zhabotinsky reaction [33, p. 371],

$$\begin{aligned} \mathrm{BrO_3^-}+\mathrm{Br^-}+2\mathrm{H^+} &= \mathrm{HBrO_2}+\mathrm{HOBr} && [1]\\ \mathrm{HBrO_2}+\mathrm{Br^-}+\mathrm{H^+} &= 2\mathrm{HOBr} && [2]\\ \mathrm{BrO_3^-}+\mathrm{HBrO_2}+\mathrm{H^+} &= 2\mathrm{BrO_2}+\mathrm{H_2O} && [3]\\ \mathrm{BrO_2}+\mathrm{M}^{n+}+\mathrm{H^+} &= \mathrm{HBrO_2}+\mathrm{M}^{(n+1)+} && [4]\\ 2\mathrm{HBrO_2} &= \mathrm{BrO_3^-}+\mathrm{HOBr}+\mathrm{H^+} && [5]\\ \mathrm{HOBr}+\mathrm{Br^-}+\mathrm{H^+} &= \mathrm{Br_2}+\mathrm{H_2O} && [6]\\ \mathrm{RH}+\mathrm{Br_2} &= \mathrm{RBr}+\mathrm{Br^-}+\mathrm{H^+} && [7]\\ \mathrm{HOBr}+\mathrm{R^\bullet} &= \mathrm{ROH}+\mathrm{Br^\bullet} && [8]\\ \mathrm{RH}+\mathrm{Br^\bullet} &= \mathrm{Br^-}+\mathrm{H^+}+\mathrm{R^\bullet} && [9]\\ \mathrm{RH}+\mathrm{M}^{(n+1)+} &= \mathrm{M}^{n+}+\mathrm{H^+}+\mathrm{R^\bullet} && [10]\\ 2\mathrm{R^\bullet}+\mathrm{H_2O} &= \mathrm{RH}+\mathrm{ROH}, && [11] \end{aligned}$$

where RH is an organic substrate, $\mathrm{R^\bullet}$ a radical belonging to RH, while M^{n+} and $\mathrm{M}^{(n+1)+}$ are metal ion catalysts; the intermediates and their numbers are $\mathrm{HBrO_2}$(1), HOBr(2), $\mathrm{Br^-}$(3), $\mathrm{M}^{(n+1)+}$(4), M^{n+}(5), $\mathrm{BrO_2}$(6), $\mathrm{Br_2}$(7), $\mathrm{Br^\bullet}$(8) and $\mathrm{R^\bullet}$(9).

11. Molecular symmetry and group theory play an important role in the quantum mechanical description of atoms and molecules [3, p. 427, 34]. To apply these tools we often need the matrices of some symmetry operations. Construct the matrices of the following operations:

(a) reflection to the plane xz in the coordinate system xyz;

(b) rotation by the angle φ around the axis x in the coordinate system xyz

(hint: the required matrix $\mathbf{A}$ appears in the equation $\mathbf{r}'=\mathbf{A}\mathbf{r}$, where $\mathbf{r}$ is an arbitrary vector and $\mathbf{r}'$ its image after the operation; $\mathbf{r}=(x,y,z)^{\mathrm{T}}$ and $\mathbf{r}'=(x',y',z')^{\mathrm{T}}$). Multiply these matrices by their respective transposes. What are the results? How do we term such matrices?

12. In the following, we give the systems of equations from which the energies and molecular orbitals of the π electrons of some particles can be determined according to Hückel method [3, p. 522]. In each case find the m values for which the given system of equation has a solution containing at least one nonzero component, and calculate the solutions themselves belonging to these m values. On the basis of the equation $m = (\alpha - E)/\beta$ determine the energies E of the particles. Knowing that β is a negative quantity, order the energies of each particle according to the increase of their magnitudes. The solutions of these systems of equations are closely related to the coefficients of the p_z atomic orbital functions in the molecular orbitals of the π electrons. The cases to be studied are as follows:

(a) Ethene

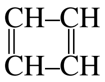
$$\begin{aligned} mc_1 + c_2 &= 0, \\ c_2 + mc_1 &= 0. \end{aligned}$$

(b) The trigonal planar radical $(CH)_3$

$$\begin{aligned} mc_1 + c_2 + c_3 &= 0, \\ c_1 + mc_2 + c_3 &= 0, \\ c_1 + c_2 + mc_3 &= 0. \end{aligned}$$

(c) The allyl radical $CH_2{=}CH{-}CH_2\cdot$

$$\begin{aligned} mc_1 + c_2 &= 0, \\ c_1 + mc_2 + c_3 &= 0, \\ c_2 + mc_3 &= 0. \end{aligned}$$

(d) The hypothetical tetragonal planar cyclobutadiene molecule 
$\begin{array}{c} CH{-}CH \\ \| \quad\;\; \| \\ CH{-}CH \end{array}$

$$\begin{aligned} mc_1 + c_2 + c_4 &= 0, \\ c_1 + mc_2 + c_3 &= 0, \\ c_2 + mc_3 + c_4 &= 0, \\ c_1 + c_3 + mc_4 &= 0. \end{aligned}$$

(e) The butadiene molecule $CH_2{=}CH{-}CH{=}CH_2$

$$\begin{aligned} mc_1 + c_2 &= 0, \\ c_1 + mc_2 + c_3 &= 0, \\ c_2 + mc_3 + c_4 &= 0, \\ c_3 + mc_4 &= 0. \end{aligned}$$

(f) The benzene molecule C_6H_6

$$\begin{aligned}
mc_1 + c_2 + c_6 &= 0,\\
c_1 + mc_2 + c_3 &= 0,\\
c_2 + mc_3 + c_4 &= 0,\\
c_3 + mc_4 + c_5 &= 0,\\
c_4 + mc_5 + c_6 &= 0,\\
c_1 + c_5 + mc_6 &= 0.
\end{aligned}$$

1.3 DERIVATIVE AND INTEGRAL

1. The Hermite polynomials, given by the general formula

$$H_n(x) = (-1)^n \mathrm{e}^{x^2} \frac{\mathrm{d}^n}{\mathrm{d}x^n} \mathrm{e}^{-x^2}; \qquad n = 0, 1, 2, \ldots \tag{1.24}$$

[1, 2, p. 60] play an important role in the description of the vibrational motion of diatomic molecules [3, p. 324].

(a) Give the first five Hermite polynomials.

(b) Verify the following statements [1, 2, pp. 60–68]:

  i. $H_n(-x) = (-1)^n H_n(x)$; $n = 0, 1, 2, \ldots$

  ii. $(\mathrm{d}/\mathrm{d}x)H_n(x) = 2nH_{n-1}(x)$; $n = 1, 2, 3 \ldots$

  iii. $H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x)$; $n = 1, 2, 3, \ldots$

  iv. $\int_{-\infty}^{\infty} H_n(x)e^{-x^2}dx = 0$; $n = 1, 2, 3, \ldots$

  v. $\int_{-\infty}^{\infty} H_n(x)H_m(x)e^{-x^2}\mathrm{d}x = \delta_{mn}2^n n!\sqrt{\pi}$; $m, n = 1, 2, 3, \ldots$

2. The Rodrigues' formula of the associated Legendre functions is

$$P_l^m(x) = (2^l l!)^{-1}(1 - x^2)^{\frac{1}{2}m} \frac{\mathrm{d}^{l+m}}{\mathrm{d}x^{l+m}}(x^2 - 1)^l, \tag{1.25}$$

where $l = 0, 1, 2, \ldots$, and $m = 0, 1, 2, \ldots, l$ [2, p. 194], [4]. This formula – in a slightly modified form required by the physical context – is included in the function that describes the spatial orbital of the electron of the hydrogenic (one-electron) atomic particles.

(a) Determine all the associated Legendre functions belonging to $l = 1, 2, 3, 4, 5$.

(b) On the basis of Eqn (1.25) show that

$$P_{l+1}^l(x) = (2l + 1)xP_l^l(x) \text{ [4]}$$

(c) What would Eqn (1.25) yield if $m > l$ were allowed?

(d) The associated Legendre functions are orthogonal in the sense that they satisfy the following equation [2, p. 201, 4]:

$$\int_{-1}^{1} P_l^m(x) P_k^m(x) = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!} \delta_{lk}.$$

Confirm this for the functions obtained in paragraph 2a in the cases of $m = 1$ and $l = 2, 4$.

3. The Rodrigues' formula of the associated Laguerre polynomials [2, p. 76, 5] is

$$L_n^k(x) = \frac{e^x x^{-k}}{n!} \frac{\mathrm{d}^n}{\mathrm{d}x^n} (e^{-x} x^{n+k}); \qquad n, k = 0, 1, 2, \ldots. \tag{1.26}$$

This appears in the parts of the orbital functions of the hydrogenic atomic particles that depend on the distance from the nucleus [3, p. 349].

(a) Calculate the $L_n^k(x)$ polynomials for $n = 1, 2, 3, 4, 5$ (let k be a parameter).

(b) The associated Laguerre-polynomials are orthogonal in the following sense [2, p. 84], [5]:

$$\int_0^\infty e^{-x} x^k L_n^k(x) L_m^k(x) \mathrm{d}x = \frac{(n+k)!}{n!} \delta_{mn}.$$

Confirm this for the polynomials $L_2^k(x)$ and $L_3^k(x)$ in paragraph 3a (k may assume any of its defined values).

4. The probability of finding for the 1s electron of a hydrogenic (one-electron) atom with atomic number Z is maximal at the nuclear distance $r \geq 0$ where the expression

$$P_{10}(r) = 4 \left(\frac{Z}{a_0} \right)^3 r^2 e^{-2Zr/a_0}$$

has a local maximum [3, p. 356]. Show that the local maximum occurs at

$$r_\mathrm{m} = \frac{a_0}{Z},$$

where $a_0 > 0$ is a constant. In the early model of the hydrogen atom by Niels Bohr the electron was moving on a circular orbit of radius a_0 around the nucleus, and this is the reason why we call a_0 Bohr radius.

5. Determine the local extrema of the following functions, which play a role in the orbitals of the hydrogenic (one-electron) atoms [3, p. 349]:

(a) $2s : \left[2 - \hat{\rho}(r)\right] e^{-(1/2)\hat{\rho}(r)}$

(b) $2p: \hat{\rho}(r)e^{-(1/2)\hat{\rho}(r)}$
(c) $3s: [27 - 18\hat{\rho}(r) + 2\hat{\rho}^2(r)]e^{-(1/3)\hat{\rho}(r)}$
(d) $3p: [6\hat{\rho}(r) - \hat{\rho}^2(r)]e^{-(1/3)\hat{\rho}(r)}$
(e) $3d: \hat{\rho}^2(r)e^{-(1/3)\hat{\rho}(r)}$.

Here $\hat{\rho}(r) = Zr/a_0$, Z is the atomic number of the hydrogenic atom, $r \geq 0$ the real distance of the electron from the nucleus, and a_0 stands for the Bohr radius (see problem 4). For the H atom ($Z = 1$) give the r values corresponding to the local extrema in picometer (pm) units as well.

6. On the basis of the definition

$$\langle r \rangle = \int_0^\infty |R_{nl}(r)|^2 r^3 \mathrm{d}r$$

calculate the average distance $\langle r \rangle$ between the electron and the nucleus for the following atomic orbitals:
(a)

$$1s\colon\ R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\hat{\rho}(r)}$$

(b)

$$2p\colon\ R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \hat{\rho}(r)e^{-(1/2)\hat{\rho}(r)}$$

(c)

$$3s\colon\ R_{30}(r) = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} [27 - 18\hat{\rho}(r) + 2\hat{\rho}^2(r)]e^{-(1/3)\hat{\rho}(r)}.$$

In these formulas $\hat{\rho}(r) = Zr/a_0 \geq 0$, $r \geq 0$ is the distance of the electron from the nucleus, $Z > 0$ the atomic number and $a_0 > 0$ the Bohr radius, respectively.

7. The quantum mechanical motion of the "particle in a box" in one dimension is described by the wave functions

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right); \qquad 0 \leq x \leq a; \quad n = 1, 2, \ldots$$

where $a > 0$ is the length of the box and x the spatial coordinate [3, p. 315].

(a) On the basis of the formula

$$\left\langle x^k \right\rangle = \int_0^a |\psi_n(x)|^2 x^k \mathrm{d}x; \qquad k = 1, 2, \ldots$$

calculate the averages $\langle x \rangle$ and $\langle x^2 \rangle$ for the particle in a box.

(b) Show that the wavefunctions of the particle in a box are orthogonal, i.e.,

$$\int_0^a \psi_i(x)\psi_j(x)\mathrm{d}x = \delta_{ij}.$$

(c) The particle in a box can be found in the interval $(x_1, x_2) \subset (0, a)$ with the probability

$$w = \int_{x_1}^{x_2} |\psi_n(x)|^2 \mathrm{d}x.$$

Calculate the value of w if

  i. $n = 1$ and the interval investigated is $(0, (1/2)a)$;
  ii. $n = 2$ and the interval investigated is $(0, (1/3)a)$; and
  iii. $n = 3$ and the interval investigated is $((1/8)a, (1/2)a)$.

8. The "particle in a box" is a model problem in quantum mechanics but it has real chemical applications too. For example, a delocalized π electron moving in a conjugated chain of carbon atoms can be viewed as a particle in a box. The variation method [35, p. 98] is one of the approximate calculation methods of quantum mechanics, by which the energy and the wavefunction of the ground state, that is, the lowest lying state, of the system investigated can be determined. Let $m > 0, E > 0, a > 0$ and $-\infty < x < \infty$ be the mass of the particle, the full mechanical energy of the particle, the length of the one-dimensional box and the spatial coordinate, respectively, and let $\hbar = h/2\pi > 0$. In order to simplify the calculations we shall use the dimensionless coordinate $\xi = x/a$ and the dimensionless energy $\varepsilon = (2ma^2/\hbar^2)E$.

(a) Let the assumed ground-state wavefunction of the particle in a box be

$$\psi(\xi, c) = \xi^c(1 - \xi),$$

where $0 \le \xi \le 1$ and $c > 1/2$ is a changeable parameter. Calculate the integrals in the formula

$$\varepsilon(c) = \frac{\int_0^1 (-\psi'')\psi \, \mathrm{d}\xi}{\int_0^1 \psi^2 \, \mathrm{d}\xi} \tag{1.27}$$

given by the variation method and give the approximate energy ε of the ground state as a function of the parameter c.

(b) According to the theory of the variation method the minimum of ε is the best approximation of the exact ground-state energy $\varepsilon_1 = \pi^2$. Differentiate ε with respect to c, calculate the value c_m at which its local minimum occurs and, to characterize the quality of the approximate value $\varepsilon(c_\mathrm{m})$, give the ratio $\varepsilon(c_\mathrm{m})/\varepsilon_1$.

9. The variation method outlined in problem 8 can also be applied to the ground state of the "harmonic oscillator" model, which plays an important role in the description of the molecular vibrations. Let $m > 0, \omega > 0, h > 0$ and $-\infty < x < \infty$ be the mass of the vibrating object, the frequency of the vibration, the Planck constant and the spatial coordinate, respectively, and let $\hbar = h/2\pi > 0$. In order to simplify the calculations we introduce the dimensionless coordinate $\xi = \sqrt{(m\omega/\hbar)}x$ and the dimensionless energy $\varepsilon = (2/\hbar\omega)E$. Let the approximate wavefunction of the ground state be

$$\psi(\xi, c) = \left(1 + c\xi^4\right) e^{-\xi^2},$$

where $-\infty < \xi < \infty$ and $-\infty < c < \infty$ is a changeable parameter.

(a) On the basis of the formula

$$\varepsilon(c) = \frac{\int_{-\infty}^{\infty} (-\psi'' + \xi^2\psi)\psi \,\mathrm{d}\xi}{\int_{-\infty}^{\infty} \psi^2 \,\mathrm{d}\xi} \tag{1.28}$$

obtained from the variation method determine the approximate energy $\varepsilon(c)$ of the ground state as a function of the parameter c.

(b) Differentiate $\varepsilon(c)$ with respect to c, calculate the value c_m at which the local minimum occurs, and compare the best approximation $\varepsilon(c_\mathrm{m})$ with the exact $\varepsilon_0 = 1$ energy of the ground state.

(Hint: For the determination of the necessary integrals use the formula)

$$\int_0^{\infty} e^{-ax^2} \mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{a}}; \quad a > 0.)$$

10. The vibrational energy levels of the diatomic molecules are reasonably well described by the formula

$$E(n) = \left(n + \frac{1}{2}\right) h\nu_\mathrm{e} - \left(n + \frac{1}{2}\right)^2 x_\mathrm{e} h\nu_\mathrm{e}; \quad n = 0, 1, 2, \ldots$$

(cf. [3, p. 480]), where $h > 0$ is the Planck constant while the constants $\nu_\mathrm{e} > 0$ and $x_\mathrm{e} > 0$ characterize the vibration of the molecule. If the vibrational quantum number n exceeds a given limit, the energy of the vibration becomes too high and the molecule dissociates.

(a) Assuming that the variable n can take any value in the interval $[0, \infty)$ determine the local maximum of E, that is, the dissociation energy D_e of the molecule.

(b) Calculate the dissociation energy D_e for the HCl molecule from the data $\nu_\mathrm{e} = 8.9875 \times 10^{13}$ Hz and $x_\mathrm{e} = 1.744 \times 10^{-2}$.

11. If we heat a closed metal container with a small hole on one of its walls ("the absolute black body"), electromagnetic radiation is emitted across the hole. The distribution of the radiation energy with respect to the wavelength – that is, the energy dE carried by the radiation of wavelengths between λ and $\lambda + \mathrm{d}\lambda$ per unit volume – is given by the expression $dE = f(\lambda)\mathrm{d}\lambda$ where, for small wavelengths,

$$f(\lambda) = \frac{8\pi hc}{\lambda^5} e^{-\frac{hc}{\lambda kT}}.$$

Here $h > 0$ is the Planck constant, $c > 0$ the speed of light in vacuum, $k > 0$ the Boltzmann constant and $T > 0$ the thermodynamical temperature [3, p. 287]. Differentiate f with respect to λ, and show that it has exactly one local extremum, which is a maximum; moreover, if the maximum occurs at λ_m then $\lambda_\mathrm{m} T$ is independent of T. (Wien displacement law).

12. The exact form of the function f in problem 11 is

$$f(\lambda) = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{(hc/\lambda kT)} - 1}$$

[3, p. 287]. In order to determine the whole energy radiated by the heated metal container (the "absolute black body") per unit volume investigate the integral

$$E = \int_0^\infty f(\lambda)\mathrm{d}\lambda.$$

(a) Using an appropriate substitution show that

$$E = 8\pi hc \left(\frac{kT}{hc}\right)^4 \int_0^\infty \frac{x^3}{e^x - 1}\mathrm{d}x, \tag{1.29}$$

that is, the whole energy of the radiation per unit volume, E, is proportional to the fourth power of the thermodynamical temperature T (Stefan–Boltzmann law).

(b) Neglecting the 1 in the denominator, approximate the integral in Eqn (1.29) by the integral

$$\int_0^\infty x^3 e^{-x}\mathrm{d}x.$$

What is the numerical value of this latter integral?

(c) After [36], use the formula

$$\frac{e^{-x}}{1-e^{-x}} = e^{-x}\sum_{k=0}^{\infty} e^{-kx} \tag{1.30}$$

originating from the sum of the infinite geometric series to estimate the integral in Eqn (1.29). For this purpose, replace the infinite series in Eqn (1.30) by the finite series $\sum_{k=0}^{n} e^{-kx}$ and calculate the transformed integral in Eqn (1.29) for $n = 1$, 5 and 10.

13. The Debye's model for the molar heat capacity $C_{\mathrm{m}V}$ of the solid metals predicts

$$C_{\mathrm{m}V} = 3Rf; \quad f(T) = 3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x-1)^2}\mathrm{d}x,$$

where $\Theta_D > 0$ is the Debye characteristic temperature, $T > 0$ the thermodynamical temperature and $R > 0$ the universal gas constant [3, p. 289]. By the numerical evaluation of the integral above calculate an approximate value for $C_{\mathrm{m}V}$ at the temperature 200 K in the case of silver (Ag), zinc (Zn) and lead (Pb). For these metals Θ_D is 225, 300 and 96 K, respectively [37, p. 936]. Use appropriate mathematical/spreadsheet software.

14. The velocity $v > 0$ of a randomly chosen gas molecule lies in the short interval $(v, v + \mathrm{d}v)$ with the probability $f(v)\mathrm{d}v$, where

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-(Mv^2/2RT)}$$

is the Maxwell distribution function for the absolute value of velocity [3, p. 27]. Here $M > 0$, $R > 0$ and $T > 0$ are the molar mass of the gas, the universal gas constant and the thermodynamical temperature, respectively.

(a) Determine by differentiation the velocity belonging to the local maximum of f. (This value is denoted by v^* and is called the most probable velocity.)

(b) What is the most probable velocity of the molecules of an N_2 gas at the temperature 300 K ($M = 28 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}$)?

(c) The average value $\langle g(v)\rangle$ of the function g depending on the velocity v is defined by

$$\langle g(v)\rangle = \int_0^{\infty} g(v)f(v)\mathrm{d}v.$$

Calculate the values of $\langle v\rangle$ and $\langle v^2\rangle$.

15. According to the van der Waals equation of state [3, p. 33] the pressure $p > 0$ of a gas depends on the temperature $T > 0$ and the molar volume $V_{\mathrm{m}} > 0$ as

$$p(V_{\mathrm{m}}, T) = \frac{RT}{V_{\mathrm{m}} - b} - \frac{a}{V_{\mathrm{m}}^2}.$$

When the temperature is fixed at the critical temperature $T_{\mathrm{c}} > 0$, the function p has an inflection point with horizontal tangent line at the critical molar volume $V_{\mathrm{mc}} > 0$. The critical pressure, $p(V_{\mathrm{mc}}, T_{\mathrm{c}})$ is briefly denoted by p_{c}. Give the relationships which connect $(p_{\mathrm{c}}, V_{\mathrm{mc}}, T_{\mathrm{c}})$ and the positive constants $(a, b$ and $R)$ in the van der Waals equation.

16. In thermodynamics the change in the molar enthalpy of a pure substance due to heating or cooling is calculated by the integral

$$\Delta H = \int_{T_1}^{T_2} C_{\mathrm{m}p}(T)\mathrm{d}T,$$

where $C_{\mathrm{m}p}(T) > 0$ is the molar heat capacity function of the given substance at constant pressure, while $T_1 > 0$ and $T_2 > 0$ are the initial and the final temperature, respectively. Let $T_1 = 273$ K and $T_2 = 373$ K. Calculate ΔH for the following cases:

(a) $\mathrm{N_2}(g) : X(x) = 27.83 + 4.19 \times 10^{-3}x$ [38, p. 568].

(b) $\mathrm{HI}(g) : X(x) = 28.29 + 2.53 \times 10^{-3}x - 5.44 \times 10^{-7}x^2$ [38, p. 573].

(c) $\mathrm{MgO}(s) : X(x) = 42.61 + 7.28 \times 10^{-3}x - 6.20 \times 10^{-5}x^{-2}$ [38, p. 574].

Here $X = C_{\mathrm{m}p}(\mathrm{J\,K^{-1}\,mol^{-1}})$ and $x = T/\mathrm{K}$ denote the numerical values (without the units) of the molar heat capacity $C_{\mathrm{m}p}$ and temperature T, respectively.

17. In thermodynamics the molar entropy change of a pure substance due to heating or cooling is determined by the integral

$$\Delta S = \int_{T_1}^{T_2} \frac{C_{\mathrm{m}p}(T)}{T}\mathrm{d}T.$$

Calculate the value of ΔS for the cases and temperature limits given in problem 16.

18. Denote $p > 0$, $V > 0$ and $T > 0$ the pressure, the volume and the temperature of a perfect gas, respectively. Assume that the pressure p of the gas changes with the volume V according to a given function $\hat{p} : (0, \infty) \to \mathbb{R}$. The curve of this function in the plane Vp is called a path. On the basis of the perfect gas

law we assign the temperature

$$\hat{T}(V) = \frac{\hat{p}(V)V}{nR} \tag{1.31}$$

to the point $(V, \hat{p}(V))$ of the given path ($n > 0$ and $R > 0$ are constants). Let $T = \hat{T}(V)$ and assume that the function $\hat{V}$ defined by $\hat{V}(T) = V$ exists and is differentiable. $\hat{V}$ is obviously the inverse of the function $\hat{T}$. The heat capacity belonging to an appropriately differentiable path is defined by

$$C(T) = C_V(T) + \hat{p}(\hat{V}(T))\frac{\mathrm{d}\hat{V}}{\mathrm{d}T}(T)$$

where $C_V(T) > 0$ is the heat capacity of the gas at constant volume. Determine the heat capacity of the perfect gas as a function of T along the paths given by

(a) $\hat{p}(V) = aV^{\alpha}$; $a > 0$, $\alpha \neq -1$;

(b) $\hat{p}(V) = p_0 \ln\left(1 + \frac{V}{V_0}\right)$; $p_0 > 0$, $V_0 > 0$.

19. Let $(p, V, T) \in I_p \times I_V \times I_T$ be the pressure, volume and temperature of a given pure substance, respectively, and let

$$f(p, V, T) = 0 \tag{1.32}$$

be a formula connecting these variables. Suppose that the functions $\hat{p} : I_V \times I_T \to I_p$ and $\hat{V} : I_p \times I_T \to I_V$ defined implicitly by Eqn (1.32) are differentiable. Furthermore, suppose that the enthalpy function $H : I_p \times I_T \to I_H$ and the internal energy function $U : I_V \times I_T \to I_U$ of the given pure substance are also defined and are differentiable. Derive two relationships between the $\frac{\partial H}{\partial T}(p, T)$ and $\frac{\partial U}{\partial T}(V, T)$ heat capacities of the pure substance in the knowledge of

(a) $H(p, T) = U(\hat{V}(p, T), T) + p\hat{V}(p, T)$;

(b) $U(V, T) = H(\hat{p}(V, T), T) - \hat{p}(V, T)V$.

20. Let $(p, V, T) \in I_p \times I_V \times I_T$ be the pressure, volume and temperature of a given pure substance, respectively, and let

$$f(p, V, T) = 0 \tag{1.33}$$

be a formula connecting these variables. Suppose that $f : I_p \times I_V \times I_T \to \mathbb{R}^3$ is a differentiable function, it has non-zero partial derivatives and the functions $\hat{p} : I_V \times I_T \to I_p$, $\hat{V} : I_p \times I_T \to I_V$ and $\hat{T} : I_p \times I_V \to I_T$ defined implicitly by Eqn (1.33) also are differentiable. Show that

$$\frac{\partial \hat{p}}{\partial V}(V, T)\frac{\partial \hat{V}}{\partial T}(p, T)\frac{\partial \hat{T}}{\partial p}(p, V) = -1$$

for the (p, V, T) triples satisfying Eqn (1.33).

21. In pure water and in dilute aqueous solutions

$$K_\mathrm{w} = [\mathrm{H}^+][\mathrm{OH}^-]$$

is valid [3, p. 230], where $[\mathrm{H}^+] > 0$ and $[\mathrm{OH}^-] > 0$ are the concentrations of the hydrogen and hydroxide ions, respectively, and $K_\mathrm{w} > 0$ is the autoprotolysis constant of water. Give $[\mathrm{H}^+] + [\mathrm{OH}^-]$ as a univariate function and show that it has a local minimum, if $[\mathrm{H}^+] = [\mathrm{OH}^-] = \sqrt{K_\mathrm{w}}$, that is, the solution is neutral.

22. In the aqueous solution of an amino acid there are $^+\mathrm{H_3N{-}R{-}COOH}$, $\mathrm{H_2N{-}R{-}COO^-}$ ions and $^+\mathrm{H_3N{-}R{-}COO^-}$ “zwitterions” in addition to the H^+ ions. Let the brief notations of these ions be $\mathrm{A}^+, \mathrm{A}^-$ and $\mathrm{A}^\pm$, respectively. The concentrations of the ions in the solution (denoted by []) fulfil the equations

$$K_1 = \frac{[\mathrm{A}^\pm][\mathrm{H}^+]}{[\mathrm{A}^+]}; \qquad K_2 = \frac{[\mathrm{A}^-][\mathrm{H}^+]}{[\mathrm{A}^\pm]};$$

$$A = [\mathrm{A}^+] + [\mathrm{A}^-] + [\mathrm{A}^\pm],$$

where $K_1 > 0$, $K_2 > 0$ and $A > 0$ are constants [39, p. 583].
(a) Give $[\mathrm{A}^\pm]$ as the function of $[\mathrm{H}^+]$ and determine by differentiation the $[\mathrm{H}^+]$ value at which $[\mathrm{A}^\pm]$ exhibits a local maximum.
(b) What can we say about the concentrations $[\mathrm{A}^+]$ and $[\mathrm{A}^-]$ at the $[\mathrm{H}^+]$ value corresponding to the local maximum of $[\mathrm{A}^\pm]$? What can be the reason for the term “isoelectric point”?

23. According to Westerlund et al. [40] in a solution containing M m-protic acids and L l-basic bases the activity of hydronium ions, x, satisfies the equation

$$x = \frac{k_1}{x} + \sum_{\nu=1}^{M} \frac{k_{2\nu}}{x} \frac{q'_\nu(1/x)}{q_\nu(1/x)} - \sum_{\nu=1}^{L} k_{3\nu} x \frac{p'_\nu(x)}{p_\nu(x)}, \tag{1.34}$$

where

$$q_\nu\left(\frac{1}{x}\right) = 1 + \sum_{i=1}^{m} \left[\prod_{j=1}^{i} k_{Aj}^{(\nu)}\right] \left(\frac{1}{x}\right)^i,$$

$$q'_\nu\left(\frac{1}{x}\right) = \sum_{i=1}^{m} i \left[\prod_{j=1}^{i} k_{Aj}^{(\nu)}\right] \left(\frac{1}{x}\right)^{i-1},$$

$$p_\nu(x) = 1 + \sum_{i=1}^{l} \left[\prod_{j=1}^{i} \frac{1}{k_{Bj}^{(\nu)}} \right] x^i,$$

$$p'_\nu(x) = \sum_{i=1}^{l} i \left[\prod_{j=1}^{i} \frac{1}{k_{Bj}^{(\nu)}} \right] x^{i-1},$$

and k_1, $k_{2\nu}$, $k_{3\nu}$, $k_{Aj}^{(\nu)}$ and $k_{Bj}^{(\nu)}$ are positive constants (q' is the derivative of the function q with respect to $1/x$).

(a) Prove that if $p(x)$ is a polynomial with positive coefficients then the function f defined by

$$f(x) = \frac{xp'(x)}{p(x)}$$

strictly monotonically increases in the interval $(0, \infty)$ [40].

(b) Utilizing the statement in paragraph 23a what can we say about the number of positive roots of Eqn (1.34)?

24. It can be shown that in the stepwise complex formation

$$\begin{aligned} \mathrm{M} + \mathrm{L} &\rightleftharpoons \mathrm{ML}, \\ \mathrm{ML} + \mathrm{L} &\rightleftharpoons \mathrm{ML}_2, \\ &\vdots \quad \vdots \\ \mathrm{ML}_{n-1} + \mathrm{L} &\rightleftharpoons \mathrm{ML}_n \end{aligned}$$

the concentrations of the metal ions M and the complex compounds ML_i $(i = 1, \ldots, n)$ depend on the concentration of the ligands L as

$$[\mathrm{M}]([\mathrm{L}]) = \frac{T_\mathrm{M}}{1 + \sum_{j=1}^{n} \beta_j [\mathrm{L}]^j},$$

$$[\mathrm{ML}_i]([\mathrm{L}]) = \frac{\beta_i T_\mathrm{M} [\mathrm{L}]^i}{1 + \sum_{j=1}^{n} \beta_j [\mathrm{L}]^j}; \quad i = 1, 2, \ldots, n,$$

where the concentrations are denoted by [] and all are positive, $T_\mathrm{M} > 0$ is the total concentration of the ligands and $\beta_j = K_1 \times K_2 \times \ldots \times K_j > 0$ $(j = 1, 2, \ldots, n)$ are the product stability constants composed of the equilibrium constants of the previous reactions [41]. Show by differentiation that for constant $T_\mathrm{M} > 0$

(a) [M] strictly monotonously decreases with the increase of [L];

(b) $[\mathrm{ML}_i]$ exhibits a unique local extremum, a local maximum, as a function of [L] for $i = 1, 2, \ldots, n-1$; furthermore $\bar{n}([L]_\mathrm{m}) = i$, where $[L]_\mathrm{m}$ is the point at which the maximum is attained and

$$\bar{n}([\mathrm{L}]) = \frac{\sum_{j=1}^{n} j\beta_j [\mathrm{L}]^j}{1 + \sum_{j=1}^{n} \beta_j [\mathrm{L}]^j}$$

is the average ligand number;

(c) $[\mathrm{ML}_n]$ strictly monotonically increases with the increase of [L].

25. In the reaction $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}$ the equilibrium mole fraction of the substance C is given by

$$x_\mathrm{C}(\xi) = \frac{x(\xi)}{1 + \xi - x(\xi)},$$

where

$$x(\xi) = \frac{1}{2}\left(1 + \xi - \sqrt{\frac{(1+\xi)^2 + K(1-\xi)^2}{K+1}}\right),$$

$0 < \xi < \infty$ is the ratio of the initial amounts of substance of B and A and $K > 0$ is the equilibrium constant of the reaction (we have assumed that C was not present in the initial reaction mixture). Show that x_C has a unique local maximum at $\xi = 1$, that is, the equilibrium mole fraction of the product is maximal when the initial amounts of the reactants correspond to the stoichiometric ratio.

26. In the consecutive first-order reaction sequence $\mathrm{A} \to \mathrm{B} \to \mathrm{C}$ the concentrations of the substances B and C vary with time as

$$b(t) = \frac{e^{-k_2 t}[a_0 k_1 + b_0(k_1 - k_2)] - a_0 k_1 e^{-k_1 t}}{k_1 - k_2}$$

and

$$c(t) = a_0 + b_0 + c_0 = \frac{a_0 k_2 e^{-k_1 t}}{k_1 - k_2} + \frac{[a_0 k_1 + b_0(k_1 - k_2)]e^{-k_2 t}}{k_2 - k_1},$$

respectively. Here $t \geq 0$ stands for time, $k_1 > 0$ and $k_2 > 0$ are the rate coefficients, which can be considered constant ($k_1 \neq k_2$), and $a_0 > 0$, $b_0 \geq 0$, $c_0 \geq 0$ the initial concentrations. Under the conditions $b_0 = 0$ and $c_0 = 0$ determine the time value for which

(a) the concentration b exhibits a local maximum; and

(b) the concentration c has an inflection point.

27. If the rate of the autocatalytic reaction $A+B \rightarrow 2B$ is

$$v = kab, \tag{1.35}$$

then the concentration vs. time functions of the two substances are given by the formulas

$$a(t) = \frac{a_0(a_0+b_0)}{b_0 e^{(a_0+b_0)kt} + a_0}; \qquad b(t) = \frac{b_0(a_0+b_0)e^{(a_0+b_0)kt}}{b_0 e^{(a_0+b_0)kt} + a_0},$$

where $t \geq 0$ is time and $k > 0, a_0 > 0$ and $b_0 > 0$ denote the rate coefficient and the two initial concentrations, respectively (k can be considered constant). Assume that $a_0 > b_0$.

(a) Calculate the value $t_m > 0$ for which function (1.35) has a local maximum.

(b) What phenomenon occurs on the curves a and b at the time t_m?

28. The matter transport caused by spatial concentration differences in a medium at rest is called diffusion. The diffusional spreading of an initially point-like matter distribution along the axis x is described by the formula

$$c(x,t) = \frac{c_0}{\sqrt{4D\pi t}} e^{-(x^2/4Dt)},$$

where $t > 0$ is the time, $-\infty < x < \infty$ the spatial coordinate, $c(x,t) > 0$ the concentration of the diffusing substance at the moment t and at the coordinate x, $c_0 > 0$ a quantity characterizing the initial distribution and $D > 0$ the diffusion coefficient, which can be treated as a constant.

(a) Differentiate the two-variable function c twice with respect to x and once with respect to t. What relationship do you find between the two derivatives?

(b) For a fixed x_0 let the function f be defined by $f(t) = c(x_0, t)$. Calculate the time value t_m for which f has a local maximum [42, Vol. 2, p. 541]. How can this method be utilized for the determination of D?

29. The propagation of an autocatalytic reaction front in a solution is similar to the spreading of a combustion front, e.g. a bush fire. If we put some autocatalyst B into a small volume element of a tube filled with the solution of substrate A, the autocatalyst will transform A into B in that volume element and, propagating via diffusion, will initiate the transformation in other volume elements too. Thus, the reaction front propagates through the system: before the front

the still unreacted solution of A, behind the front the products of the reaction, including B, can be found. In the following we shall apply the approach of Showalter and Tyson [43] in a slightly generalized form. Let us investigate the propagating reaction front in the reaction

$$\mathrm{A} + m\mathrm{B} \to p\mathrm{B} + \mathrm{P}; \qquad v = g(a)b; \quad p - m > 0$$

(where v is the reaction rate; $g > 0$ a function defined on $(0, \infty)$, which is known from the experiments; $a, b > 0$ the concentrations of A and B, respectively). Assume that a is held at the constant value a_0 by an external flow. Then, along the axis x and at the moment t, the concentration of the autocatalyst B can be given by the formula

$$b(x,t) = \frac{b_0 e^{(p-m)g(a_0)t} e^{-(x^2/4Dt)}}{\sqrt{4\pi Dt}}; \quad -\infty < x < \infty; \qquad t > 0, \qquad (1.36)$$

where $D > 0$ is the diffusion coefficient of the autocatalyst B and $b_0 > 0$ a quantity charaterizing the point-like inital distribution of B. (The quantities $p - m$, D, a_0, $g(a_0)$ and b_0 can all be treated as constants.)

(a) Suppose that B becomes observable in the system when its concentration exceeds a threshold value $b_c > 0$. On the basis of Eqn (1.36) determine the positive function x_c defined by $b(x_c(t), t) = b_c$. This function describes the migration of the point along the axis x, which instantaneously corresponds to the concentration b_c.

(b) Determine the propagation velocity $\mathrm{d}x_c/\mathrm{d}t$ of the autocatalytic reaction front by the differentiation of x_c with respect to t.

30. According to the geometric theory by Volford et al. [44] when a planar reaction front propagates from the point P to the point Q it “chooses” the ray from the set of rays connecting the two points along which the propagation time is minimal (cf. Fermat’s principle on the propagation of light). Fig. 1.1 shows a situation when a propagating planar reaction front enters a new medium where the direction and the velocity of its propagation change. The propagation time along the ray shown in the figure is

$$\begin{aligned} T(x) &= \frac{s_1}{v_1} + \frac{s_2}{v_2} \\ &= \frac{\sqrt{x^2 + a^2}}{v_1} + \frac{\sqrt{(c-x)^2 + b^2}}{v_2}; \qquad 0 < x < c, \end{aligned}$$

where $v_1 > 0$ and $v_2 > 0$ are the propagating velocities in the two media.

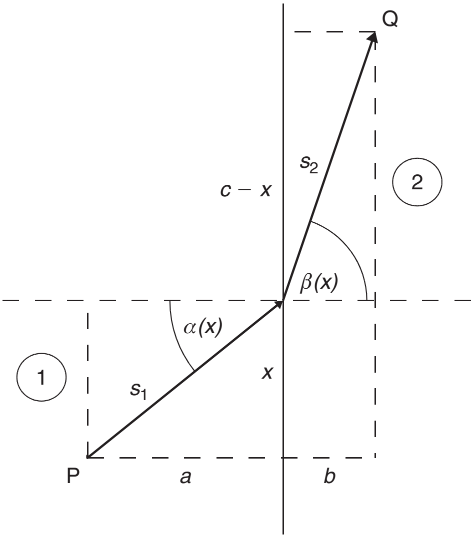


Figure 1.1 A propagating planar reaction front at the border of media 1 and 2; P: starting point; Q: end point

(a) Show that if $T'(x_\mathrm{m}) = 0$ then

$$\frac{\sin\alpha(x_\mathrm{m})}{\sin\beta(x_\mathrm{m})} = \frac{v_1}{v_2}$$

[44] and $T''(x_\mathrm{m}) > 0$ (for α and β see Fig. 1.1).

(b) Show that there exists exactly one x_m for which $T'(x_\mathrm{m}) = 0$.

31. We investigate a reaction system in which the concentrations $(c_1, c_2, \ldots, c_n) \in \mathbb{R}_+^n$ change in time according to the rate expressions $(f_1, f_2, \ldots, f_n) : \mathbb{R}_+^n \to \mathbb{R}^n$. After Szili and Tóth [45, 46] we say that a reaction system contains cross-inhibition at the concentration vector $(\bar{c}_1, \bar{c}_2, \ldots, \bar{c}_n) \in \mathbb{R}_+^n$ if there exists a pair of integers (i,j) $(i \neq j)$ for which $\partial_j f_i(\bar{c}_1, \bar{c}_2, \ldots, \bar{c}_n) < 0$. Which of the following systems contain cross inhibition at some $(\bar{c}_1, \bar{c}_2, \ldots, \bar{c}_n) \in \mathbb{R}_+^n$:

(a)

$$f_1(c_1, c_2) = k_1 c_1 - k_2 c_1 c_2,$$
$$f_2(c_1, c_2) = k_2 c_1 c_2 - k_3 c_2,$$

where $k_1, k_2, k_3 > 0$ are constants [6, 7];

(b)

$$\begin{aligned} f_1(c_1,c_2,c_3) &= -c_1c_2^2 + \eta_1 c_2^3 + \alpha(1-c_1), \\ f_2(c_1,c_2,c_3) &= c_1c_2^2 - \eta_1 c_2^3 - k_2(c_2 - \eta_2 c_3), \\ f_3(c_1,c_2,c_3) &= k_2(c_2 - \eta_2 c_3) - \alpha c_3, \end{aligned}$$

where $\alpha, \eta_1, \eta_2, k_2 > 0$ are constants [47];

(c)

$$\begin{aligned} f_1(c_1,c_2,c_3) &= a_1c_2 - a_2c_1 - a_4a_5\left(a_3c_1 + \frac{c_1}{1+c_1+a_6c_1^2}\right), \\ f_2(c_1,c_2,c_3) &= a_7 - a_8c_2 - \frac{c_2}{(1+c_2+a_9c_2^2)(1+c_3)}, \\ f_3(c_1,c_2,c_3) &= a_{10}\left[\frac{c_2}{(1+c_2+a_9c_2^2)(1+c_3)}\right. \\ &\qquad \left. + a_5\left(a_3c_1 + \frac{c_1}{1+c_1+a_6c_1^2}\right) - a_{11}c_3 - a_{12}\right], \end{aligned}$$

where $a_1, a_2, \ldots, a_{12}$ are positive constants [48];

(d)

$$f_i(c_1,c_2,\ldots,c_n) = \sum_{j=1}^{n} k_{ij}c_j; \qquad i = 1,2,\ldots,n,$$

where k_{ij} $(i,j = 1,2,\ldots,n)$ are constants and $k_{ij} \geq 0$ if $i \neq j$ [45, 46]?

32. We measured the concentration of a reagent solution n times and – as a result of the random experimental errors – obtained the concentration values $c_1, c_2, \ldots, c_n > 0$. According to the principle of least squares [30, p. 1285] the most probable concentration of the solution is the value c^* at which the function f defined by

$$f(c) = \sum_{i=1}^{n} (c_i - c)^2; \qquad c > 0$$

attains its unique local minimum. Differentiate the function f, and give the relationship between c^* and the parameters $c_1, c_2, \ldots, c_n$.

33. The light absorption of a solution layer is usually characterized by the absorbance $A > 0$. At a given wavelength the absorbance A of a solution

depends on the concentration $c > 0$ of the light absorbing species as $A = \varepsilon c l$, where the molar absorbance $\varepsilon > 0$ and the thickness of the solution layer $l > 0$ are both constants. When we measure the absorbances of the solutions of concentrations $c_1, c_2, \ldots, c_n$, the obtained absorbance values are $A_1, A_2, \ldots, A_n$, respectively. Assume that only $A_1, A_2, \ldots, A_n$ contain experimental errors, and let $x = \varepsilon l$. According to the principle of least squares [30, p. 1285] the most probable value of x is the value x^* at which the function f defined by

$$f(x) = \sum_{i=1}^{n} (A_i - c_i x)^2; \qquad x > 0$$

attains its unique local minimum. Determine x^* by the differentiation of the function f.

34. According to Kohlrausch law [3, p. 738] the molar conductivity $\Lambda_\mathrm{m} > 0$ of a dilute solution of a strong electrolyte depends on the concentration $c > 0$ as

$$\Lambda_\mathrm{m} = \Lambda_\mathrm{m}^0 - A\sqrt{c},$$

where Λ_m^0 is the molar conductivity of the infinitely dilute solution and A is a proportionality coefficient (both Λ_m^0 and A can be considered constant). When we measure the molar conductivities of the solutions of concentrations $c_1, c_2, \ldots, c_n$, we obtain the results $\Lambda_{\mathrm{m}1}, \Lambda_{\mathrm{m}2}, \ldots, \Lambda_{\mathrm{m}n}$, respectively. Assume that only $\Lambda_{\mathrm{m}1}, \Lambda_{\mathrm{m}2}, \ldots, \Lambda_{\mathrm{m}n}$ are affected by the experimental errors, and let $x = \Lambda_\mathrm{m}^0$ and $y = A$. According to the principle of least squares [30, p. 1285] the most probable values of x and y are the corresponding coordinates of the point (x^*, y^*) at which the function f defined by

$$f(x,y) = \sum_{i=1}^{n} (x - y\sqrt{c_i} - \Lambda_{\mathrm{m}i})^2; \qquad x, y > 0$$

attains its unique local minimum. Calculate x^* and y^* by the differentiation of the funcion f.

35. In order to extract the solute from the solvent A we use the solvent B which does not mix with A. We add B to the original solution, and wait until the solute is distributed among the two solvent phases layered on each other. Then we remove the phase containing B. Suppose that we perform three extractions with the volumes $V_1 > 0$, $V_2 > 0$ and $V_3 > 0$ of the solvent B, waiting each time until the partition equilibrium concerning the solute is achieved. It can

be shown that in this case the full amount of the solute passed to the phases of solvent B is

$$n(V_1, V_2, V_3) = \frac{c_A}{K}\left[\frac{V_1}{1+\frac{V_1}{KV_A}} + \frac{V_2}{\left(1+\frac{V_1}{KV_A}\right)\left(1+\frac{V_2}{KV_A}\right)} + \frac{V_3}{\left(1+\frac{V_1}{KV_A}\right)\left(1+\frac{V_2}{KV_A}\right)\left(1+\frac{V_3}{KV_A}\right)}\right], \quad (1.37)$$

where $c_A > 0$ is the initial concentration of the solute in the solvent A, $V_A > 0$ the volume of solvent A and $K > 0$ the partition ratio, which is assumed to be constant. Let the full volume,

$$V = V_1 + V_2 + V_3, \quad (1.38)$$

of the solvent B be constant. Prove that the full extracted amount of the solute is maximal if the three extraction volumes of solvent B are equal. Apply the following two methods:

(a) Express V_3 from Eqn (1.38) and substitute the result into Eqn (1.37). Give the domain of definition and the local extrema of the two-variable function obtained.

(b) Deal with the extremum problem of the three-variable function given by Eqn (1.37) using Lagrange multipliers.

1.4 SEQUENCES, SERIES AND LIMITS

1. At the same external pressure the boiling point of a dilute solution of a non-volatile solute is always higher than that of the pure solvent. According to the theoretical considerations [3, p. 178] the difference between the boiling point of the solution and that of the pure solvent, $\Delta T(x) > 0$, obeys the relationship

$$\Delta T(x) = -\frac{RT^{*2}}{\Delta H}\ln(1-x),$$

where $0 < x \ll 1$ is the mole fraction of the solute, $T^* > 0$ the boiling point of the pure solvent, $\Delta H > 0$ the enthalpy of vaporization of the pure solvent, finally $R > 0$ the universal gas constant. By the help of L'Hospital's rule show that

$$\lim_{x \to 0} \frac{\Delta T(x)}{x} = \frac{RT^{*2}}{\Delta H}.$$

2. Suppose that a substance is partially soluble in both of the immiscible solvents (1) and (2). If we add solvent (2) to a solution made with solvent (1) some solute will migrate to solvent (2) and a partition equilibrium will be reached. Since the two solvent phases do not mix with each other the solvent phase (2) containing the extracted solute can be removed easily. Let c_1^0 be the initial concentration of the solute in a volume $V_1 > 0$ of the solvent phase (1). Suppose we extract the solute from the solvent phase (1) in i steps by adding a volume $V/i > 0$ of the solvent (2) to the volume V_1 of the solvent phase (1). It can be shown that the extracted amounts of the solute form a geometric sequence, and after i steps the amount of substance for the extracted solute, n_i, is given by

$$n_i = c_1^0 V_1 \left[1 - \frac{1}{\left(1 + \frac{V}{iKV_1}\right)^i} \right]; \qquad i = 1, 2, \ldots,$$

where $K > 0$ is the partition ratio, which can be considered constant. What can we say about the boundedness and monotonicity of the sequence $\{n_i\}$? Determine the limit of the sequence for $i \to \infty$.

3. When the weak acid HA dissociates in a dilute solution the concentration of the H^+ ions in the solution, $[H^+]$, can be given by the positive root of the equation

$$\left\{\frac{[H^+](c)}{c^\ominus}\right\}^3 + K_a \left\{\frac{[H^+](c)}{c^\ominus}\right\}^2 - \left(K_a \frac{c}{c^\ominus} + K_w\right) \left\{\frac{[H^+](c)}{c^\ominus}\right\} - K_a K_w = 0, \tag{1.39}$$

where $c > 0$ is the concentration of the solution, $K_a > 0$ the dissociation constant of the acid, $K_w > 0$ the autoprotolysis constant of water and $c^\ominus$ the unit of concentration. Show that

$$\lim_{c \to \infty} \left\{[H^+](c) - [H^+]_2(c)\right\} = 0,$$

where $[\mathrm{H}^+]_2(c)$ is the positive solution of the equation

$$\left\{\frac{[\mathrm{H}^+]_2(c)}{c^{\ominus}}\right\}^2 + K_\mathrm{a}\left\{\frac{[\mathrm{H}^+]_2(c)}{c^{\ominus}}\right\} - K_\mathrm{a}\frac{c}{c^{\ominus}} = 0. \tag{1.40}$$

4. According to Westerlund et al. in a solution containing M m-protic acids and L l-basic bases the activity x of the hydroxonium ions fulfils the equation

$$x = \frac{k_1}{x} + \sum_{\nu=1}^{M}\frac{k_{2\nu}}{x}\frac{q'_\nu(1/x)}{q_\nu(1/x)} - \sum_{\nu=1}^{L} k_{3\nu}x\frac{p'_\nu(x)}{p_\nu(x)}, \tag{1.41}$$

where

$$q_\nu\left(\frac{1}{x}\right) = 1 + \sum_{i=1}^{m}\left[\prod_{j=1}^{i} k_{Aj}^{(\nu)}\right]\left(\frac{1}{x}\right)^i,$$

$$q'_\nu\left(\frac{1}{x}\right) = \sum_{i=1}^{m} i\left[\prod_{j=1}^{i} k_{Aj}^{(\nu)}\right]\left(\frac{1}{x}\right)^{i-1},$$

$$p_\nu(x) = 1 + \sum_{i=1}^{l}\left[\prod_{j=1}^{i}\frac{1}{k_{Bj}^{(\nu)}}\right]x^i,$$

$$p'_\nu(x) = \sum_{i=1}^{l} i\left[\prod_{j=1}^{i}\frac{1}{k_{Bj}^{(\nu)}}\right]x^{i-1},$$

finally k_1, $k_{2\nu}$, $k_{3\nu}$, $k_{Aj}^{(\nu)}$ and $k_{Bj}^{(\nu)}$ are all positive constants [40]. Determine the limits of the right-hand side of Eqn (1.41) if $x \to 0$ and $x \to \infty$, and, on the basis of the results, show that Eqn (1.41) has a positive root [40].

5. When vapour is adsorbed on the surface of a solid, it is reasonable to assume that the full adsorbed layer will consist of several monomolecular layers since each adsorbed monomolecular layer has some capacity to bind a new layer. This effect is taken into account by the sign $\sum$ in the Brunauer–Emmett–Teller (BET) adsorption isotherm

$$\frac{n^\sigma(x)}{n^\sigma_\mathrm{m}} = \frac{c\sum_{i=1}^{\infty} ix^i}{1 + c\sum_{i=1}^{\infty} x^i} \tag{1.42}$$

[49, p. 174]. In this equation $n^{\sigma}(x) > 0$ and $n^{\sigma}_{\mathrm{m}} > 0$ stand for the total adsorbed amount of vapour and the monolayer capacity, respectively; in the variable $x = (p/p^*)$ $(0 < x < 1)$ $p > 0$ is the pressure of the vapour above the solid surface and $p^* > 0$ the saturated vapour pressure at the given temperature; finally $c > 0$ is a constant.

(a) Give the right-hand side of Eqn (1.42) after the accomplishment of the indicated summations. (Hint: identify the type of the infinite series in the denominator. Differentiate this series and try to relate the result to the infinite series in the numerator.)

(b) What happens if $x \to 1$ (that is, $p \to p^*$) in Eqn (1.42)?

6. If we layer some water onto a sugar solution, the sugar migrates via diffusion into the pure water, and after a sufficiently long time period, its concentration becomes spatially uniform. If the total length of the solution + water layers is denoted by L, the concentration c of the diffusing sugar is given by the formula

$$c(x,t) = \sum_{n=0}^{\infty} B_n e^{-\frac{n^2\pi^2 D}{L^2}t} \cos\left(\frac{n\pi x}{L}\right), \tag{1.43}$$

where $x > 0$ is the height measured from the bottom of the sugar solution, $t \geq 0$ the time and $D > 0$ the diffusion coefficient of the sugar, which can be considered constant. At the start of the experiment the length and the concentration of the sugar solution are $L_0 > 0$ and $c_0 > 0$, respectively. Expand the initial concentration vs. x function into a Fourier series and determine the coefficents B_n. Give the limit of c if $t \to \infty$ at a fixed value of x. (Suppose that the limit of the infinite series (1.43) can be obtained as the sum of the limits of the individual terms.)

7. Suppose we fill a long horizontally fixed tube with water and then put some sugar solution into the water at the cooordinate $x = 0$. The spatiotemporal migration of the sugar via diffusion from the origin can be described by the equation

$$c(x,t) = \frac{c_0 e^{-(x^2/4Dt)}}{\sqrt{4\pi D t}},$$

where $c(x,t)$ is the concentration of the sugar, $-\infty < x < \infty$ the spatial coordinate, $t > 0$ the time, $c_0 > 0$ a constant characterizing the concentration of the sugar solution in the initial narrow region and $D > 0$ the diffusion coefficient of the sugar, which can also be considered constant. Using this formula show that – in accordance with the chemical expectations – $c(x,t) \to 0$, if $t \to 0$ for any fixed $x \neq 0$.

8. We fill a long horizontal tube with the solution of the substrate A, and add some solution of the autocatalyst B to the substrate solution at the coordinate $x = 0$. After some time we observe two autocatalytic reaction fronts that propagate in the positive and negative directions of the axis x. The fronts move towards the regions of the untouched substrate A and gradually transform the latters into the product of the reaction, the autocatalyst B; behind the reaction front the solution of B can be found. We study this phenomenon using the approach of Showalter and Tyson [43]. If the net equation and the rate equation of the autocatalytic reaction are

$$\mathrm{A} + \mathrm{B} \to 2\mathrm{B}; \qquad v = k[\mathrm{A}][\mathrm{B}],$$

and the concentration of A is held at the constant value $[\mathrm{A}]_0 > 0$ then the spatiotemporal concentration distribution of the autocatalyst B can be given by the equation

$$[\mathrm{B}](x,t) = \frac{[\mathrm{B}]_0 e^{k[\mathrm{A}]_0 t - (x^2/4Dt)}}{\sqrt{4\pi D t}}, \tag{1.44}$$

where x is the spatial coordinate, $t > 0$ the time, $[\mathrm{B}]_0 > 0$ a quantity characterizing the initial distribution of the autocatalyst and $D > 0$ the diffusion coefficient of the autocatalyst ($[\mathrm{B}]_0$ and D can also be considered constant). From Eqn (1.44) it is possible to determine the velocity $v(t) > 0$ with which the point $x_\mathrm{r}(t)$ corresponding to the fixed concentration $[\mathrm{B}]_\mathrm{r} > 0$ wanders along the axis x, and the result is

$$v(t) = \sqrt{\frac{D}{2}} \frac{\left\{ \ln \frac{[\mathrm{B}]_0^2}{4\pi D t [\mathrm{B}]_\mathrm{r}^2} + 4[\mathrm{A}]_0 k t - 1 \right\}}{\sqrt{t \ln \frac{[\mathrm{B}]_0^2}{4\pi D t [\mathrm{B}]_\mathrm{r}^2} + 2[\mathrm{A}]_0 k t^2}}.$$

Find the limit $v_\infty = \lim_{t\to\infty} v(t)$. Let $D = 10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ and $[\mathrm{A}]_0 = 0.1\,\mathrm{mol\,dm}^{-3}$. Give the rate coefficent k for which the front velocity v_∞ would be equal to the average velocity of the world champion of the (say men's) 100 m sprint.

9. In an ultracentrifuge [3, p. 686] rotating with the angular velocity ω around a vertical axis the horizontal movement of the macromolecules away from the axis is described by the formula

$$r(\xi,t) = A_1 e^{\alpha_1(\xi)t} + A_2 e^{\alpha_2(\xi)t} \neq 0, \tag{1.45}$$

where r is the distance of the macromolecule from the axis, A_1 and A_2 the nonzero constants determined by the initial position and velocity, $t \geq 0$ the time, $\alpha_1(\xi)$ and $\alpha_2(\xi)$ the positive and negative solutions of the quadratic equation

$$\alpha^2(\xi) + \frac{1}{\xi}\alpha(\xi) - \left(1 - \frac{\rho^*}{\rho}\right)\omega^2 = 0, \tag{1.46}$$

finally $\rho > \rho^* > 0$ are the densities of the medium and the particle, respectively. The parameter ξ is defined by $\xi = (m/k) > 0$, where $m > 0$ is the mass of the particle, and $k > 0$ is the coefficient of the frictional force acting on the moving particle.

(a) On the basis of Eqn (1.45) determine the limit

$$\lim_{t\to\infty} \frac{1}{r(\xi,t)} \frac{\mathrm{d}r}{\mathrm{d}t}(\xi,t)$$

for fixed values of ξ.

(b) Give the limit

$$\lim_{\xi\to 0} \frac{\alpha(\xi)}{S(\xi)}$$

where $\alpha(\xi)$ is the limit obtained in paragraph 9a and

$$S(\xi) = \left(1 - \frac{\rho^*}{\rho}\right)\xi.$$

10. Electron diffraction is a useful method for the investigation of the structures of different materials. Here the intensity distribution $I(s)$ of the electrons scattered on the atoms of a molecule is given by the formula

$$I(s) = \sum_{i=1}^{n}\sum_{j=1}^{n} f_i f_j \frac{\sin sr_{ij}}{sr_{ij}},$$

where n is the number of the atoms in the molecule, f_i and f_j are the scattering coefficients of the ith and the jth atoms, respectively, r_{ij} the distance of the two atoms and s the independent variable of the function I, which is proportional to the angle betwen the original and the diverted electron beams [3, p. 643]. In the case of $i = j$ the terms in the double sum are defined by the limit

$$\lim_{r_{ii}\to 0} \frac{\sin sr_{ii}}{sr_{ii}}$$

for $s \neq 0$. Find this limit.

11. According to quantum mechanics, which is applied to the description of the motions of atomic particles, the wavefunction for a spherical stationary state of a particle in a sphere [50] is defined by the formula

$$\psi(r) = \frac{A}{r}\sin\alpha r + \frac{B}{r}\cos\alpha r.$$

Here the variable $r > 0$ is the radial distance while $\alpha \neq 0$, A and B are real constants. For what values of A and B will ψ have a finite limit when $r \to 0$?

12. According to quantum mechanics the possible energies of a given vibration of a molecule are $E_0 = (1/2)h\nu$, $E_1 = (3/2)h\nu$, $E_2 = (5/2)h\nu$, ..., that is,

$$E_i = \left(i + \frac{1}{2}\right)h\nu; \qquad i = 0, 1, 2, \ldots,$$

where $\nu > 0$ is the frequency of the vibration and $h > 0$ the Planck constant [3, p. 600]. The partition function Z – with the energies measured from the smallest energy level $E_0 = (1/2)h\nu$ – is given by the formula

$$Z(\nu, T) = \sum_{i=0}^{\infty} e^{-(ih\nu/kT)},$$

where $k > 0$ is the Boltzmann constant and $T > 0$ the thermodynamical temperature [3, p. 600].

(a) Find the type of the infinite series $Z(\nu, T)$ and give the sum of the series.

(b) Applying L'Hospital's rule to the sum in paragraph 12a give the limit

$$\lim_{T\to\infty} \frac{h\nu}{kT} Z(\nu, T)$$

for constant values of ν.

13. The energy of the radiation emitted by an ideally black body per unit volume and unit wavelength is given by

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{(hc/\lambda kT)} - 1}\right),$$

where $k > 0$ is the Boltzmann constant, $T > 0$ the thermodynamical temperature, π the well-known mathematical constant, $\lambda > 0$ the wavelength of the radiation, $h > 0$ the Planck constant and $c > 0$ the speed of light in vacuum [3, p. 287]. Employing L'Hospital's rule show that for fixed values of T

(a)

$$\lim_{\lambda\to 0} \rho(\lambda, T) = 0;$$

(b)

$$\lim_{\lambda\to\infty}\frac{\hat{\rho}(\lambda,T)}{\rho(\lambda,T)}=1,$$

where

$$\hat{\rho}(\lambda,T)=\frac{8\pi kT}{\lambda^4}. \tag{1.47}$$

If $\hat{\rho}(\lambda,T)$ were the formula that correctly describes the energy density of the black body radiation in the full wavelength range then the energy density would be very high for small wavelengths, the energies of the objects would be radiated to space rapidly and so an "ultraviolet catastrophe" would occur. Nevertheless, in the early 20th century classical physics was only able to produce Eqn (1.47) revealing thereby its limitations.

14. The Debye's model for the molar heat capacity $C_{\mathrm{m}V}$ of the solid metals predicts

$$C_{\mathrm{m}V}=3Rf;\quad f(T)=3\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3\int_0^{\Theta_{\mathrm{D}}/T}\frac{x^4e^x}{(e^x-1)^2}\mathrm{d}x,$$

where $\Theta_{\mathrm{D}}>0$ is the Debye characteristic temperature, $T>0$ the thermodynamical temperature and $R>0$ the universal gas constant [3, p. 289]. Calculate the following limits by the L'Hospital's rule:

(a)

$$\lim_{x\to 0}\frac{x^4e^x}{(e^x-1)^2}.$$

(b)

$$\lim_{T\to\infty}f(T).$$

15. In a fictitious one-dimensional ionic crystal KA the positive and the negative ions alternate regularly along a straight line, the distance of two adjacent ions is constant. For the determination of the full electrostatic interaction energy of the ions we must calculate the Madelung constant M of the crystal lattice defined by

$$\frac{1}{2}M=\sum_{i=1}^{\infty}\frac{(-1)^{i+1}}{i}. \tag{1.48}$$

Give the sum of the infinite series on the right-hand side of Eqn (1.48) by the following methods:

(a) Expand the expression $\ln(1+x)$ into a Taylor series around $x=0$, and find the value of x for which the obtained series agrees with the one in Eqn (1.48).

(b) Since we know from Leibniz criterion that the infinite series in Eqn (1.48) is convergent, for the determination of its sum it is sufficient to find the limit of the $2n$th partial sums as $n \to \infty$.

  i. Show by mathematical induction that the formula for the $2n$th partial sums is

$$a_{2n} = \frac{1}{n+1} + \frac{1}{n+2} + \cdots + \frac{1}{2n}$$

  ($n = 1, 2, 3, \dots$) (cf., for example, [51, p. 61]).

  ii. Find two sequences, $\{b_n\}$ and $\{c_n\}$, for which

$$\lim_{n\to\infty} b_n = \lim_{n\to\infty} c_n = A$$

  is known and which ensure via the relations

$$b_n \leq a_{2n} \leq c_n$$

  that

$$\lim_{n\to\infty} a_{2n} = A.$$

  (Hint: use that the indefinite integral of $1/(x+b)$ is $\ln|x+b| + C$.)

16. For the determination of the full electrostatic interaction energy of the ions in the crystal lattice of NaCl we must determine the Madelung constant

$$M = -\sum_{i^2+j^2+k^2\neq 0} \frac{(-1)^{i+j+k}}{\sqrt{i^2+j^2+k^2}} \tag{1.49}$$

(i, j and k are integers). It is not unambiguous, however, how this three-dimensional infinite series should be summarized since its convergence depends on the order of its terms [52–54]. Using the method of "expanding cubes" we obtain a convergent series with the sum

$$M = 1.7475\dots \tag{1.50}$$

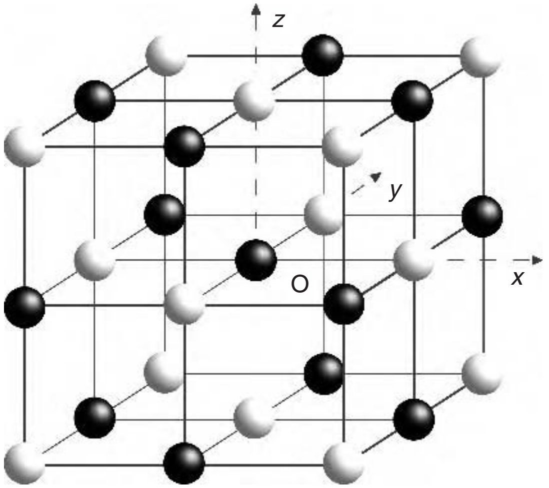


Figure 1.2 A cube of edge length 2; O: origin; black: $i+j+k$ is even; white: $i+j+k$ is odd

[52–54]. According to this method, for the determination of the first, second, third, etc. partial sums we symmetrically draw cubes with edge lengths 2,4,6, etc. around the origin and sum the contributions (see Eqn (1.49)) of the points (i,j,k) that belong to these cubes. If the contributions of the points on the faces, edges and vertices of the cubes are taken into account by the weights $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{8}$, respectively, then the sequence of the partial sums will converge relatively quickly to the previous value of M [55]. Determine the first and the second partial sums by the method of "expanding cubes". Apply the weights given previously. Compare these partial sums with the value of M given in Eqn (1.50). Use Fig. 1.2 if necessary.

17. According to quantum mechanics the possible energies of the one-dimensional translational motion of a gas molecule are given by the formula

$$\varepsilon_n = \frac{n^2h^2}{8ma^2}; \qquad n = 1, 2, \ldots,$$

where $h > 0$ is the Planck constant, $m > 0$ the mass of the particle and $a > 0$ the length of the gas container. The partition function

$$q(\beta\varepsilon) = \sum_{n=1}^{\infty} e^{-\beta(\varepsilon_n - \varepsilon)} = \sum_{n=1}^{\infty} e^{-(n^2-1)\beta\varepsilon}, \tag{1.51}$$

where

$$\varepsilon = \frac{h^2}{8ma^2}, \quad \beta = \frac{1}{kT},$$

$k > 0$ is the Boltzmann constant and $T > 0$ is the thermodynamical temperature, plays an important role in the microscopic explanation of the macroscopic properties of gases [3, p. 577].

(a) For fixed values of $\beta\varepsilon > 0$ prove (using, for example, the ratio test) that the infinite series in Eqn (1.51) is convergent.

(b) Using appropriate integrals give an upper estimate and a lower one for the kth partial sum of Eqn (1.51), and show that

$$2q(\beta\varepsilon)\sqrt{\frac{\beta\varepsilon}{\pi}} \to 1$$

if $\beta\varepsilon \to 0$.

1.5 DIFFERENTIAL EQUATIONS

1. We shall investigate a first-order decay reaction with the stoichiometric equation A → P.

(a) Let the concentration of the substance A be [A]. The temporal change of [A] is described by the initial value problem

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k[\mathrm{A}]; \qquad [\mathrm{A}](0) = [\mathrm{A}]_0$$

where $t \geq 0$ is time, $k > 0$ the rate coefficient and $[\mathrm{A}]_0 > 0$ the initial value of [A] (k and $[\mathrm{A}]_0$ can be considered constant). Find the solution [A] of this initial value problem defined on the interval $0 \leq t < \infty$.

(b) Let the concentration of the substance P be [P]. The temporal change of [P] is described by the initial value problem

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k[\mathrm{A}]; \qquad [\mathrm{P}](0) = [\mathrm{P}]_0,$$

where [A] is the function obtained in paragraph 1a, $[\mathrm{P}]_0 \geq 0$ the initial value of [P] and the other quantities are given in paragraph 2a. Find the solution [P] of this initial value problem defined on the interval $0 \leq t < \infty$.

(c) Show that

$$[\mathrm{A}](t) + [\mathrm{P}](t) = [\mathrm{A}]_0 + [\mathrm{P}]_0$$

for $0 \le t < \infty$.

(d) The half-life $t_{1/2}$ of the decay is the duration during which [A] decreases to the value $([\mathrm{A}]_0)/2$. Determine this quantity.

2. We shall investigate an nth-order decay reaction with the stoichiometric equation A → P.

   (a) Let the concentration of the substance A be [A]. The temporal change of [A] undergoes the initial value problem

   $$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k[\mathrm{A}]^n; \qquad [\mathrm{A}](0) = [\mathrm{A}]_0,$$

   where $t \ge 0$ is time, $k > 0$ the rate coefficient, the integer $n > 1$ the order of the decay and $[\mathrm{A}]_0 > 0$ the initial value of [A] (the last three quantities are constants). Find the solution [A] of this initial value problem defined on the interval $0 \le t < \infty$.

   (b) Let the concentration of the substance P be [P]. The temporal change of [P] is governed by the initial value problem

   $$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k[\mathrm{A}]^n; \qquad [\mathrm{P}](0) = [\mathrm{P}]_0,$$

   where [A] is the function determined in the paragraph 1a, $[\mathrm{P}]_0 \ge 0$ the initial value of [P] and the other quantities are given in pragraph 2a. Find the solution [P] of this initial value problem defined on the interval $0 \le t < \infty$.

   (c) Show that

   $$[\mathrm{A}](t) + [\mathrm{P}](t) = [\mathrm{A}]_0 + [\mathrm{P}]_0$$

   for $0 \le t < \infty$.

   (d) The half-life $t_{1/2}$ is defined in the previous problem. Determine the half-life of the decay in the present case.

3. We shall investigate the temporal concentration change of the intermediate B in a first-order consecutive reaction system with the stoichiometric equations A → B → C. Let the concentration of the substance B be [B]. The temporal change of [B] can be determined from the initial value problem

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k[\mathrm{A}] - k'[\mathrm{B}]; \qquad [\mathrm{B}](0) = [\mathrm{B}]_0,$$

where $t \geq 0$ is time, [A] the function obtained in paragraph 1a, $k > 0$ and $k' > 0$ are the rate coefficients and $[B]_0 \geq 0$ the initial concentration of [B] (the last three quantities can be considered constant). Find the solution [B] of this initial value problem defined on the interval $0 \leq t < \infty$. For completeness, deal with the chemically irrealistic case of $k = k'$ too.

4. We shall investigate a second-order reaction with the stoichiometric equation $A + B \rightarrow P$. Let the concentrations of the substances A and B be [A] and [B], respectively. The temporal changes of [A] and [B] can be determined from the initial value problem

$$\begin{aligned} \frac{d[A]}{dt} &= -k[A][B]; & \frac{d[B]}{dt} &= -k[A][B], \\ [A](0) &= [A]_0; & [B](0) &= [B]_0, \end{aligned} \tag{1.52}$$

where $t \geq 0$ is time, $k > 0$ the rate coefficient and $[A]_0 > 0$ and $[B]_0 > 0$ are the initial concentrations (the last three quantities can be treated as constants).

(a) Show that

$$[A] - [B] = [A]_0 - [B]_0, \tag{1.53}$$

is valid in the entire domain of definition of the solution ([A],[B]), and – by the help of Eqns (1.52) and (1.53) – derive a separate differential equation for [A].

(b) Find the solution [A] of the differential equation derived in paragraph 4a that is defined on the interval $0 \leq t < \infty$ and fulfils the initial condition $[A](0) = [A]_0$.

5. We shall study the autocatalytic reaction $A + 2B \rightarrow 3B$ in which the temporal evolution of the system is given by the initial value problem

$$\begin{aligned} \frac{d[A]}{dt} &= -k[A][B]^2; & \frac{d[B]}{dt} &= k[A][B]^2, \\ [A](0) &= [A]_0; & [B](0) &= [B]_0, \end{aligned} \tag{1.54}$$

where [A] and [B] are the concentrations of the substances A and B, $t \geq 0$ is time, $k > 0$ the rate coefficient finally $[A]_0 > 0$ and $[B]_0 > 0$ the initial values of [A] and [B].

(a) Show that

$$[A] + [B] = [A]_0 + [B]_0 \tag{1.55}$$

is fulfilled in the entire domain of definition of the solution ([A],[B]), and – using Eqns (1.54) and (1.55) – derive a separate differential equation for [B].

(b) Find the solution [B] of the differential equation derived in paragraph 5a that is defined on the interval $0 \leq t < \infty$ and satisfies the initial condition $[\mathrm{B}](0) = [\mathrm{B}]_0$.

6. We shall investigate a first-order reversible decay reaction whose stoichiometric equation is $\mathrm{A} \rightleftharpoons \mathrm{B}$. Let the concentrations of the substances A and B be [A] and [B], respectively. The temporal changes of [A] and [B] are given by the initial value problem

$$\begin{aligned} \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} &= -k[\mathrm{A}] + k'[\mathrm{B}]; & \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} &= k[\mathrm{A}] - k'[\mathrm{B}], \\ [\mathrm{A}](0) &= [\mathrm{A}]_0; & [\mathrm{B}](0) &= [\mathrm{B}]_0, \end{aligned} \tag{1.56}$$

where $t \geq 0$ is time, $k > 0$, $k' > 0$ are the rate coefficients and $[\mathrm{A}]_0 > 0$ and $[\mathrm{B}]_0 > 0$ the initial concentrations.

(a) Show that

$$[\mathrm{A}] + [\mathrm{B}] = [\mathrm{A}]_0 + [\mathrm{B}]_0 \tag{1.57}$$

is fulfilled in the entire domain of definition of the solution ([A], [B]), and – on the basis of Eqns (1.56) and (1.57) derive a separate differential equation for [A].

(b) Find the solution of the differential equation derived in paragraph 6a that is defined on the interval $0 \leq t < \infty$ and satisfies the initial condition $[\mathrm{A}](0) = [\mathrm{A}]_0$. Then – using Eqn (1.57) – give the function [B] too.

(c) Calculate the limit $\lim_{t \to \infty} [\mathrm{B}](t)/[\mathrm{A}](t)$. What is the chemical importance of the result?

7. Suppose that the concentration of the substance X can be described by the differential equation

$$\dot{x}(t) = -f(t)x(t) + g(t)$$

where f and g are continuous functions on the interval $[0, \alpha)$ $(\alpha > 0)$, moreover $g(t) \geq 0$ for any $0 \leq t < \alpha$. Let x be a solution of this differential equation that is defined on the interval $[0, \alpha)$. Show that $x(t) > 0$ for any $0 < t < \alpha$ if $x(0) > 0$ (In general the positivity of the solutions of the kinetic differential equations is related to the lack of "negative cross-effects" [56].).

8. Assume that the concentration b of the substance B in the reaction system $\mathrm{A} \to \mathrm{B}; \quad 2\mathrm{B} \to \mathrm{P}$ satisfies the differential equation

$$\frac{\mathrm{d}b}{\mathrm{d}t}(t) = k_1 a_0 e^{-k_1 t} - 2k_2 b^2(t), \tag{1.58}$$

where $t \geq 0$ stands for time, $k_1 > 0$, $k_2 > 0$ stand for the rate coefficients and $a_0 > 0$ stands for the initial concentration of the substance A (the last three quantities can be considered constant). Show that any solution b of Eqn (1.58) can exhibit at most one local extremum, and this extremum must be a maximum.

9. In a first-order consecutive reaction system with the stoichiometric equations $B_1 \rightarrow B_2 \rightarrow \cdots \rightarrow B_N$ ($N \geq 3$) the concentrations of the substances $B_1, B_2, \ldots, B_N$ (denoted by $b_1, b_2, \ldots, b_N$, respectively) are described by the system of differential equations

$$\dot{b}_1 = -k_1 b_1; \qquad \dot{b}_2 = k_1 b_1 - k_2 b_2; \ldots$$
$$\dot{b}_{N-1} = k_{N-2} b_{N-2} - k_{N-1} b_{N-1}; \qquad \dot{b}_N = k_{N-1} b_{N-1},$$

where $k_1, k_2, \ldots, k_{N-1}$ are the positive rate coefficients, which can be considered constant. Let $(b_1, b_2, \ldots, b_N)$ be an arbitrary solution of this system. Show that the function b_i $(i = 1, 2, \ldots, N)$ from $(b_1, b_2, \ldots, b_N)$ can have at most $i - 1$ local extrema.

10. In the Lotka–Volterra model [6, 7]

$$\begin{aligned} A + X &\rightarrow 2X, \\ X + Y &\rightarrow 2Y, \\ Y &\rightarrow P, \end{aligned}$$

the concentrations of the substances X and Y ($x > 0$ and $y > 0$, respectively) are described by the system of differential equations

$$\begin{aligned} \dot{x} &= k_1' a x - k_2 x y, \\ \dot{y} &= k_2 x y - k_3 y, \end{aligned} \tag{1.59}$$

where $a > 0$ is the concentration of the substance A while $k_1' > 0$, $k_2 > 0$ and $k_3 > 0$ are the rate coefficients that can be considered constant. Assume that a is also held at a constant value by an appropriate external matter flow, and let $k_1 = k_1' a$.

(a) Show that the function F given by

$$F(u, v) = u^{k_3} v^{k_1} e^{-k_2(u+v)}; \qquad u, v > 0 \tag{1.60}$$

is a first integral of the system (1.59).

(b) Show that the curves $F(u, v) = c$ are closed if the values of c are taken from an appropriate interval $(0, p)$. Give a possible positive value of p.

(This feature suggests that the positive solutions of Eqn (1.59) defined on $0 \leq t < \infty$ are periodic functions.)

11. Dancsó and Farkas [57] have shown that there exist chemical reaction systems in which the periodic concentration changes can be described approximately by the differential equations

$$\begin{aligned} \dot{x} &= K_1 - K_2 y, \\ \dot{y} &= K_3 x - K_4, \end{aligned} \tag{1.61}$$

where $x > 0$ and $y > 0$ represent the concentrations of some substances while K_1, K_2, K_3 and K_4 are positive constants. Determine the frequency of the periodic solutions of Eqn (1.61). (Hint: reduce the system to a single differential equation of known type and investigate the solutions of the latter.)

12. Assume that the pressure, the volume and the temperature of the investigated reaction system are all costants and there is no matter transport between the system and its surroundings. Then the concentrations of the substances in the system ($c_i > 0$; $i = 1, 2, \dots, N$) are described by the continuously differentiable system of differential equations

$$\dot{c}_i(t) = \sum_{j=1}^{R} \nu_{ij} w_j(c_1(t), c_2(t), \dots, c_N(t)) \qquad i = 1, 2, \dots, N, \tag{1.62}$$

where $t \geq 0$ is time, R the number of the reactions, ν_{ij} the stoichiometric coefficient of the ith substance in the jth reaction and w_j the rate of the jth reaction. The coefficients ν_{ij} satisfy the "reaction equations"

$$\sum_{i=1}^{N} \nu_{ij} M_i = 0; \qquad j = 1, 2, \dots, R,$$

where the non-zero quantities $M_1, M_2, \dots, M_N$ are the "molar masses". Prove that

(a) $F(u_1, u_2, \dots, u_N) = \sum_{i=1}^{N} M_i u_i$ is a first integral of system (1.62);

(b) Let $(c_1, c_2, \dots, c_N)$ be a solution of Eqn (1.62). Show that if $\dot{c}_\xi$ is of constant sign on the entire domain of definition of c_ξ then the functions c_i $(i \neq \xi)$ cannot be all periodic with the same period.

13. Suppose that the right-hand side of the system of differential equations

$$\dot{c}_i(t) = f_i(c_1(t), c_2(t), \dots, c_N(t)); \qquad i = 1, 2, \dots, N \tag{1.63}$$

is defined on an open set $W \subset \mathbb{R}^N$ and is continuously differentiable there. Many chemical reaction systems are described by such differential systems.

Eqn (1.63) is called a gradient system if

$$f_i(u_1, u_2, \ldots, u_N) = \frac{\partial V}{\partial u_i}(u_1, u_2, \ldots, u_N) \quad i = 1, 2, \ldots, N,$$

where V is a given function of the variable $(u_1, u_2, \ldots, u_N) \in \mathbb{R}^N$. Prove that if Eqn (1.63) is a gradient system then it does not have a non-constant periodic solution.

14. In a continuously stirred tank reactor (c.s.t.r.) the concentrations of the substances, $c_i > 0 \quad (i = 1, 2, \ldots, N)$, are described by the initial value problem

$$\begin{aligned} \dot{c}_i(t) &= f_i(c_1(t), c_2(t), \ldots,\ c_N(t)) + k_0[c_{i0} - c_i(t)], \\ c_i(0) &= c_i^0, \\ i &= 1, 2, \ldots, N, \end{aligned} \tag{1.64}$$

where $t \geq 0$ is time, $k_0 > 0$ and $c_{i0} \geq 0$ are constants characteristic of the reactor and $c_i^0 > 0$ the initial concentrations. The continuously differentiable f_i scalar functions describe the kinetics of the reactions taking place in the system. Assume that at least one of the quantities c_{i0} is not zero and that there exist some positive constants $M_1, M_2, \ldots, M_N$ (the "molar masses") with which

$$\sum_{i=1}^{N} M_i f_i = 0.$$

(a) Show that in this case

$$\lim_{t \to \infty} f(t) = \sum_{i=1}^{N} M_i c_{i0}$$

is fulfilled for the function f defined by

$$f(t) = \sum_{i=1}^{N} M_i c_i(t),$$

where $(c_1\, c_2 \ldots, c_N)$ is any solution defined on the interval $[0, \infty)$.

(b) What can be said about the boundedness of the solutions $(c_1\, c_2 \ldots c_N)$ on the basis of paragraph 14a?

(c) Is

$$f(t) = \sum_{i=1}^{N} M_i c_{i0}$$

valid for the entire domain of definition of f if $(c_1\ c_2 \ldots c_N)$ is a periodic solution defined on the interval $[0, \infty)$? Why?

15. If R reversible reactions take place in a system comprised of N substances then the concentrations $c_i > 0$ of the substances – as functions of time $t \geq 0$ – can be described by the system of differential equations

$$\dot{c}_i = \sum_{j=1}^{R} (\nu_{+ij} - \nu_{-ij})(v_{-j} - v_{+j}); \qquad i = 1, 2, \ldots, N, \tag{1.65}$$

where $\nu_{-ij} \geq 0$ and $\nu_{+ij} \geq 0$ are the stoichiometric coefficients of the ith substance in the jth reaction as a reactant and a product, respectively,

$$v_{-j}(c_1, c_2, \ldots c_N) = k_{-j} \prod_{i=1}^{N} c_i^{\nu_{-ij}}$$

and

$$v_{+j}(c_1, c_2, \ldots c_N) = k_{+j} \prod_{i=1}^{N} c_i^{\nu_{+ij}}$$

are the rates of the direct and the reverse processes of the jth reaction, respectively, finally $k_{+j} > 0$ and $k_{-j} > 0$ are the rate coefficients, which can be considered constant. Suppose that the principle of detailed balance is valid for the positive concentrations $(\bar{c}_1, \bar{c}_2, \ldots, \bar{c}_N)$, that is,

$$v_{-j}(\bar{c}_1, \bar{c}_2, \ldots, \bar{c}_N) = v_{+j}(\bar{c}_1, \bar{c}_2, \ldots, \bar{c}_N), \quad j = 1, 2, \ldots, R.$$

Let $(c_1, c_2, \ldots, c_N)$ be a non-constant solution of Eqn (1.65). Show for the function g defined by

$$g(t) = \sum_{i=1}^{N} \left[c_i(t) \ln\left(\frac{c_i(t)}{\bar{c}_i}\right) - c_i(t) + \bar{c}_i \right]$$

that on its entire interval of definition

$$\dot{g}(t) < 0$$

[58, 59]. What can we say about the existence of a non-constant periodic solution of Eqn (1.65) defined on $[0, \infty)$?

16. Merkin et al. [60] extensively studied the temporal behaviour of the version

$$\begin{aligned} \mathrm{P} &\to \mathrm{A}, \\ \mathrm{A} + 2\mathrm{B} &\to 3\mathrm{B}, \\ \mathrm{B} &\to \mathrm{C} \end{aligned}$$

of the Autocatalator model. When the concentration of P is constant, this model is described by the dimensionless differential equations

$$\begin{aligned} \dot{x} &= \mu - xy^2, \\ \dot{y} &= xy^2 - y, \end{aligned} \tag{1.66}$$

where the unknown functions $x > 0$ and $y > 0$ are proportional to the concentrations of A and B, respectively, and the parameter $\mu > 0$ includes the rate coefficients and the concentration of P (μ can be considered constant). By the aid of mathematical/spreadsheet software determine numerically the solution (x, y) of Eqn (1.66) starting from the initial condition $x(0) = 0.11$ and $y(0) = 0.95$ for the case of $\mu = 0.95$. Plot the solution as a function of time $t \geq 0$ in the interval $[0, 150]$. In addition, plot the $(x(t), y(t))$ pairs in the coordinate system xy. What conclusion can you draw from the figures obtained?

17. Under appropriate conditions shrinking red rings appear on the blue surface of a Belousov–Zhabotinsky reaction mixture poured in a Petri dish. According to the theory, the temporal change of the radius $r > 0$ of a ring is given by the initial value problem

$$\frac{\mathrm{d}r}{\mathrm{d}t} = -\frac{D}{r}; \qquad r(0) = r_0 > 0, \tag{1.67}$$

where $t \geq 0$ is time and $D > 0$ the diffusion coefficient, which can be considered constant [61].
    (a) Solve this initial value problem.
    (b) According to the experiments the red rings initially shrink slowly but then disappear quickly. Explain this on the basis of Eqn (1.67).

18. If we apply an electrostatic field to a solution (electrolysis) then the ions in the solution start to move towards the electrodes as a result of the electrical force acting on them. At the same time, however, the ions are braked by a frictional force proportional to their velocity. According to Newton's second

law the motion of a positive ion of electric charge $q > 0$ and mass $m > 0$ along the axis x is described by the initial value problem

$$\ddot{x}(t) + \frac{k}{m}\dot{x}(t) = \frac{q}{m}E; \qquad x(0) = x_0; \quad \dot{x}(0) = v_0, \tag{1.68}$$

where $t \geq 0$ is time, $k > 0$ the proportionality coefficient of the frictional force, $E > 0$ the strength of the homogeneous electrostatic field finally x_0 and v_0 are the initial position and velocity of the ion, respectively (the last four quantities can be considered constant).

(a) Find the solution of Eqn (1.68) defined on $0 \leq t < \infty$.

(b) Give the stationary velocity of the ion, that is, $v_\infty = \lim_{t\to\infty} \dot{x}(t)$. How much time is needed by a SO_4^{2-} ion that is initially at rest to reach the velocity $0.9v_\infty$? For this ion $m = 1.6 \times 10^{-25}$ kg and $k = 3.9 \times 10^{-12}$ ns m^{-1}.

19. In the cell of an ultracentrifuge [3, p. 686] rotating by the angular velocity ω the particles of the macromolecular solute move away from the axis of rotation under the effects of the centrifugal force, the “buoyancy force” occurring in the centrifugal field and the frictional force proportional to the particle’s velocity. On the basis of Newton’s second law the instantaneous distance $r > 0$ of a particle of mass $m > 0$ from the axis of rotation can be determined from the initial value problem

$$\ddot{r}(t) + \frac{k}{m}\dot{r}(t) - \left(1 - \frac{\rho^*}{\rho}\right)\omega^2 r(t) = 0; \qquad r(0) = r_0; \quad \dot{r}(0) = v_0,$$

where $t \geq 0$ is time, $k > 0$ the proportionality coefficient of the frictional force, $\rho > \rho^*$ the density of the solute particles and $\rho^* > 0$ the density of the solution. Find the solution of this initial value problem defined on $0 \leq t < \infty$.

20. During a very slow change of the state of a perfect gas in a thermally insulated container [3, p. 63] the connection between the volume $V > 0$ and the temperature $T > 0$ of the gas is described by the initial value problem

$$(1 - \kappa)\frac{\mathrm{d}V}{\mathrm{d}T}(T) = \frac{V(T)}{T}; \qquad V(T_0) = V_0, \tag{1.69}$$

where $\kappa > 1$ is a dimensionless quantity and $T_0 > 0$ and $V_0 > 0$ are the initial temperature and volume, respectively (these three quantities can be considered constant).

(a) Find the solution of Eqn (1.69) defined on $0 < T < \infty$.

(b) Using the function determined in paragraph 20a and the perfect gas law $pV = nRT$ give the pressure $p > 0$ of the process investigated as a function of the temperature $T > 0$ and then as a function of the volume $V > 0$ ($n > 0$ and $R > 0$ are constants).

(c) At 298 K temperature the volume of a perfect gas in a thermally insulated container is $2\,\mathrm{m}^3$. Give the temperature of the gas if we very slowly expand it to the volume $2.5\,\mathrm{m}^3$ ($\kappa = 5/3$).

21. According to quantum mechanics the motion of a particle confined to an one-dimensional box with a very rigid wall is described by the boundary value problem

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\alpha^2\psi; \qquad \psi(0) = \psi(a) = 0,$$

where ψ is the wavefunction of the particle, x the space coordinate, $a > 0$ the length of the box, $\alpha^2 = (\frac{2m}{\hbar^2})E$, $m > 0$ and $E > 0$ are the mass and the total mechanical energy of the particle, respectively (a and m are constants).

(a) Find the solutions ψ of this boundary value problem that are not identically zero. For which values of E do such solutions exist?

(b) Each not identically zero solution contains an arbitrary multiplying constant. Determine this constant so that

$$\int_0^a |\psi|^2\,\mathrm{d}x = 1$$

be valid ("normed wavefunction").

22. The differential equation

$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2}(x) - 2x\frac{\mathrm{d}y}{\mathrm{d}x}(x) + 2ny(x) = 0, \tag{1.70}$$

where $-\infty < x < \infty$ and $n = 0, 1, 2, \ldots$ is closely related to the quantum mechanical description of the vibration of diatomic molecules [62, 63, p. 66].

(a) Suppose that the polynomial

$$y_n(x) = \sum_{k=0}^{n} a_i x^i$$

is a solution of Eqn (1.70). What is the relationship between the coefficients a_i?

(b) On the basis of the previous paragraph give the solution functions y_n for $n = 0, 1, 2, 3, 4, 5, 6$.

(c) Compare the obtained solutions y_n with the following formula of Hermite polynomials [1, 2, p. 60]:

$$H_n(x) = (-1)^n e^{x^2} \frac{\mathrm{d}^n}{\mathrm{d}x^n} e^{-x^2}.$$

What do you find?

23. The differential equation

$$x\frac{\mathrm{d}^2 y}{\mathrm{d}x^2}(x) + (k+1-x)\frac{\mathrm{d}y}{\mathrm{d}x}(x) + ny(x) = 0, \tag{1.71}$$

where $0 < x < \infty$ and $n, k = 0, 1, 2, \ldots$ (for the general case see [2, p. 80, 5]) is closely related to the quantum mechanical description of the one-electron ("hydrogenic") atomic particles [3, p. 345].

(a) Assume that the polynomial

$$y_n(x) = \sum_{i=0}^{n} a_i x^i$$

is a solution of Eqn (1.71). What is the relationship between the coefficients a_i? (For the sake of simplicity we do not mark the dependence of y_n on k.)

(b) Determine the concrete forms of the solutions y_n for $n = 0, 1, 2, 3$ (let k be a parameter).

(c) Compare the y_n solutions obtained in the previous paragraph with the Rodrigues' formula of the associated Laguerre polynomials [5],

$$L_n^k(x) = \frac{e^x x^{-k}}{n!} \frac{\mathrm{d}^n}{\mathrm{d}x^n}(e^{-x}x^{n+k}).$$

What do you find?

24. Scott et al. [64] described the stationary temperature distribution in the inside of a spherical catalyst particle by the boundary value problem

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\rho^2}(\rho) + \frac{2}{\rho}\frac{\mathrm{d}\theta}{\mathrm{d}\rho}(\rho) + \delta\alpha^5[1+\mu\theta(\rho)]^5 = 0; \quad 0 < \rho < 1, \tag{1.72}$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}\rho}(0) = 0; \quad \theta(1) = 0, \tag{1.73}$$

where θ is the dimensionless temperature, ρ the dimensionless distance measured from the centre of the particle finally $\alpha > 0$, $\delta > 0$ and $\mu > 0$ are dimensionless constants.

(a) Demonstrate that by the substitutions

$$\rho = \hat{\rho}(z) = (\delta\alpha^5\mu)^{-1/2}z; \qquad \phi(z) = 1 + \mu\theta(\hat{\rho}(z))$$

Eqns (1.72) and (1.73) become

$$\frac{d^2\phi}{dz^2}(z) + \frac{2}{z}\frac{d\phi}{dz}(z) + \phi^5(z) = 0; \qquad 0 < z < z^*, \tag{1.74}$$

$$\frac{d\phi}{dz}(0) = 0; \qquad \phi(z^*) = 1, \tag{1.75}$$

where $z^* = (\delta\alpha^5\mu)^{1/2}$.

(b) Determine the relationship between the parameters a and b if the function ϕ defined by

$$\phi(z) = \left(\frac{a}{b + z^2}\right)^{1/2} \tag{1.76}$$

is a solution of Eqn (1.74) and satisfies the boundary condition at $z = 0$ in Eqn (1.75).

(c) Determine the remained parameter in Eqn (1.76) such that ϕ also fulfils the boundary condition at $z = z^*$ in Eqn (1.75).

25. The boundary value problem

$$\frac{d^2\hat{u}}{dx^2} = -\delta e^{\hat{u}}; \qquad 0 \le x \le 1, \tag{1.77}$$

$$\frac{d\hat{u}}{dx}(0) = 0; \qquad \hat{u}(1) = 0, \tag{1.78}$$

which is now considered as a special case of the Liouville–Bratu–Gelfand problem [65] in mathematics, was applied by Frank-Kamenetsky [66] for the study of the temperature distribution in a one-dimensional chemically reacting system. In this problem one end of the system ($x = 0$) is thermally insulated while at the other ($x = 1$) the quantity $\hat{u}$ proportional to temperature is kept at a constant value. The constant $\delta > 0$ characterizes the quantity of heat produced by the chemical reaction.

(a) Let $\phi > 0$ be a solution of the boundary value problem

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = -\lambda\phi; \quad 0 \le x \le 1, \tag{1.79}$$

$$\frac{\mathrm{d}\phi}{\mathrm{d}x}(0) = 0; \qquad \phi(1) = 0, \tag{1.80}$$

with $\lambda > 0$. Show [65] that the problem (1.77) and (1.78) has a solution only if $\delta \le \lambda$. (Hint: multiply both sides of Eqn (1.77) by ϕ then integrate both sides by parts. On the right-hand side apply $\hat{u} \le e^{\hat{u}}$.)

(b) Solve Eqns (1.79) and (1.80), and give a number as an upper bound for the δ values that ensure the existence of a solution $\hat{u}$ of Eqns (1.77) and (1.78).

(c) Find the general solution of Eqn (1.77) containing two arbitrary constants.

(d) Prove that there exists a threshold value δ_c with the following property: for $\delta < \delta_c$ the boundary condition at $x = 1$ can be satisfied by two values of one of the constants in the general solution, that is, there are two solutions, while for $\delta > \delta_c$ this boundary condition cannot be fulfilled by any real constant, so Eqns (1.79) and (1.80) do not have any solution (see also [65]).

(e) Give the value δ_c and characterize the sharpness of the estimation obtained in paragraph 25b.

26. Let $p > 0$, $V > 0$ and $T > 0$ be the pressure, the volume and the temperature of a perfect gas, respectively. It follows from the general laws of thermodynamics that p – as a function of V and T – satisfies the partial differential equation

$$\frac{\partial p}{\partial T}(V,T) = \frac{p(V,T)}{T} \tag{1.81}$$

on a positive rectangle of the plane VT. Show that the perfect gas equation

$$p(V,T) = \frac{nRT}{V}$$

is a solution of Eqn (1.81) ($n > 0$ is the amount of substance and $R > 0$ the universal gas constant, both are constants in a mathematical sense). Can you give another positive function p that also satisfies Eqn (1.81)?

27. In the two-dimensional version of the quantum mechanical problem "particle in a box" [3, p. 319] we have to solve the boundary value problem

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{2mE}{\hbar^2}\psi,$$

$$\psi(0,y) = \psi(a,y) = 0; \qquad \psi(x,0) = \psi(x,b) = 0,$$

$$0 \le x \le a; \qquad 0 \le y \le b,$$

where $\psi, m > 0$ and $E > 0$ are the wavefunction, the mass and the total mechanical energy of the particle, respectively, $\hbar > 0$ a constant, x and y the space coordinates finally $a > 0$ and $b > 0$ are the edge lengths of the box.

(a) Find the not identically zero solutions of this problem by the separation of variables, that is, assume the solutions in the form

$$\psi(x,y) = X(x)Y(y). \tag{1.82}$$

(b) How many solutions do belong to a given value of E if $a \neq b$? What is the answer if $a = b$?

28. A solution of the diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}; \qquad t > 0; \quad -\infty < x < \infty \tag{1.83}$$

has the form

$$c(x,t) = f\left(\frac{x}{2\sqrt{Dt}}\right) \tag{1.84}$$

[67, p. 279] ($c > 0$: concentration; $D > 0$: diffusion coefficient, can be considered constant; x: space coordinate; t: time). Substitute Eqn (1.84) into Eqn (1.83), and determine the function f from the ordinary differential equation obtained.

29. The spatiotemporal change of the concentration c of a substance diffusing on an infinite line obeys the initial value problem

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}; \qquad t > 0; \quad -\infty < x < \infty,$$

$$c(x,0) = \phi(x),$$

where x is the space coordinate, t is time, $D > 0$ the diffusion coefficient, which can be regarded as constant, and ϕ a bounded function giving the initial spatial distribution of c. The solution of this problem is given by the general formula [67, p. 244]

$$c(x,t) = \frac{1}{\sqrt{4D\pi t}} \int_{-\infty}^{\infty} \phi(\alpha) e^{-((x-\alpha)^2/4Dt)} \mathrm{d}\alpha. \tag{1.85}$$

(a) Introduce the new variable

$$\xi = \frac{x-\alpha}{\sqrt{4Dt}}$$

into Eqn (1.85), and express the solutions with the “error function”, erf [68], defined by

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} \mathrm{d}\eta; \qquad -\infty < z < \infty \tag{1.86}$$

in the following cases ($a > 0$, $c_0, c_1, c_2 > 0$ are all constants):

i.

$$\phi(x) = \begin{cases} c_1 & \text{if } x < 0, \\ c_2 & \text{if } x \geq 0, \end{cases}$$

ii.

$$\phi(x) = \begin{cases} c_0 & \text{if } |x| \leq a, \\ 0 & \text{if } |x| > a, \end{cases}$$

iii.

$$\phi(x) = \begin{cases} c_0 \left(1 - \frac{|x|}{a}\right) & \text{if } |x| \leq a, \\ 0 & \text{if } |x| > a. \end{cases}$$

(b) In the relatively simple cases 29(a)i and 29(a)ii show by differentiation that the solutions obtained really satisfy the differential equation.

(c) Demonstrate that each solution c fulfils the initial condition in the following sense: if ϕ is continuous at the point x_0 then

$$\lim_{t \to 0} g(t) = \phi(x_0)$$

for the function g defined by

$$g(t) = c(x_0, t).$$

30. Consider an inhomogeneous solution in a very long and thin horizontal tube, and suppose that the concentration c of the diffusing solute is kept at the zero value at one side of the system. Then the concentration c – as the function of time t and the space coordinate x – is governed by the problem

$$\begin{aligned} \frac{\partial c}{\partial t} &= D\frac{\partial^2 c}{\partial x^2}; \quad t > 0, \quad 0 < x < \infty, \\ c(x,0) &= \phi(x), \\ c(0,t) &= 0, \end{aligned}$$

where $D > 0$ is the diffusion coefficient, which can be considered constant, and ϕ a bounded function. The general formula of the solution of this problem is [67, p. 257]

$$c(x,t) = \frac{1}{\sqrt{4D\pi t}} \int_0^\infty \phi(\alpha) \left[e^{-((x-\alpha)^2/4Dt)} - e^{-((x+\alpha)^2/4Dt)} \right] \mathrm{d}\alpha.$$

(a) Introducing the new integration variables

$$\xi = \frac{x-\alpha}{\sqrt{4Dt}}; \qquad \eta = \frac{x+\alpha}{\sqrt{4Dt}} \tag{1.87}$$

and the function erf (see Eqn (1.86)) determine the concentration of the diffusing solute if $\phi(x) = c_0 > 0$.

(b) Show by differentiation that the solution found in paragraph 30a really satisfies the differential equation.

(c) Assume that we know the concentration gradient in the bounding plane:

$$\frac{\partial c}{\partial x}(0,t) = \gamma,$$

where γ is a constant. Determine the time that has elapsed since the start of the diffusion experiment corresponding to paragraph 30a. (Lord Kelvin estimated the age of the Earth from the analogous heat conduction problem [67, p. 272].)

31. In the one-dimensional system of length $L > 0$ described by the problem

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + kb_0 c, \quad t > 0, \quad 0 < x < L, \tag{1.88}$$

$$c(x,0) = c_0 > 0, \tag{1.89}$$

$$c(0,t) = c(L,t) = 0 \tag{1.90}$$

[67, p. 519] a substance is produced with the rate kb_0c and then some part of this substance migrates to the ends of the system via diffusion and leaves the system ($c \geq 0$: the concentration of the substance; $D > 0$: diffusion coefficient; x: space coordinate; t: time; $k > 0$: rate coefficient; $b_0 > 0$: the concentration of the reaction partner; ϕ: a bounded function giving the initial concentration distribution; D, k and b_0 are constants.)

(a) Assume the solution of Eqns (1.88)–(1.90) in the form $c(x,t) = u(x,t)f(t)$. What form must f have if we want u to be the solution of the problem

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2}, \quad t > 0, \quad 0 < x < L, \tag{1.91}$$

$$u(x,0) = c_0 > 0, \tag{1.92}$$

$$u(0,t) = u(L,t) = 0? \tag{1.93}$$

(b) By the method of separation of variables find the not identically zero functions of the form $X(x)T(t)$ that solve the boundary value problem consisting of Eqns (1.91)–(1.93).

(c) Find the solution of the differential equation (1.91) that satisfies the initial condition (1.92) besides the boundary conditions (1.93). (Hint: create an infinite linear combination of the solutions obtained in paragraph 31b. In order to determine the unknown coefficients in this linear combination expand Eqn (1.92) into a Fourier series.)

(d) In the knowledge of f and the solution u of Eqns (1.91)–(1.93) determine the solution c of Eqns (1.88)–(1.90). Show that the concentration of the produced substance, c, becomes unbounded as a function of t if

$$L > \pi\sqrt{\frac{D}{kb_0}}.$$

[67, p. 520] (the problem models an explosion that occurs when the size of the system exceeds a critical limit).

32. The reaction–diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + kb_0c; \qquad t > 0; \quad -\infty < x < \infty \tag{1.94}$$

describes the formation and diffusional migration of a substance in an infinitely long one-dimensional system, the rate of the formation is kb_0c

(see the notation in problem 31). By a “wave solution” of this equation we mean a solution of the form

$$c(x,t) = f(x+vt); \qquad -\infty < x < \infty, \quad t > 0, \tag{1.95}$$

where $v \neq 0$ is a constant. (The origin of the term: the curve of such a solution as the function of x is translated along the axis x with the velocity v as t increases.)

(a) Let $\xi = x + vt$. Show that

$$D\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2}(\xi) - v\frac{\mathrm{d}f}{\mathrm{d}\xi}(\xi) + kb_0 f(\xi) = 0; \qquad -\infty < \xi < \infty. \tag{1.96}$$

(b) Let

$$f(\xi) = Pe^{\lambda_1 \xi} + Qe^{\lambda_2 \xi}; \qquad (P, Q > 0)$$

be a solution of Eqn (1.96) for which $f(\xi) \to 0$ as $\xi \to \infty$ and $f(\xi) \to \infty$ as $\xi \to -\infty$. What can you say about the value v belonging to this solution?

33. Following Kaliappan [69] find the values $B \neq 0$ and $v \neq 0$ for which the function f defined by

$$f(\xi) = (1 + Ae^{-B\xi})^{-2}; \qquad A > 0$$

is a solution of the dimensionless boundary value problem

$$f''(\xi) - vf'(\xi) + f(\xi)[1 - f(\xi)] = 0; \qquad -\infty < \xi < \infty,$$

$$f(-\infty) = 0; \qquad f(\infty) = 1$$

describing the spatial form of some chemical waves.

34. After Gray et al [70] determine the values $k \neq 0$ and $v \neq 0$ for which the function f defined by

$$f(\xi) = (1 + Ke^{-k\xi})^{-1}; \qquad K > 0$$

is a solution of the dimensionless boundary value problem

$$2f''(\xi) + vf'(\xi) + f^2(\xi)[1 - f(\xi)] = 0 \quad -\infty < \xi < \infty$$

$$f(-\infty) = 1; \quad f(\infty) = 0$$

describing the spatial form of some chemical waves.

35. After Benguria and Depassier [71] consider the boundary value problem

$$\frac{\mathrm{d}^2\hat{q}}{\mathrm{d}\xi^2}(\xi) + v\frac{\mathrm{d}\hat{q}}{\mathrm{d}\xi}(\xi) + f(\hat{q}(\xi)) = 0; \tag{1.97}$$

$$\lim_{\xi\to-\infty} \hat{q}(\xi) = 1; \qquad \lim_{\xi\to\infty} \hat{q}(\xi) = 0, \tag{1.98}$$

which gives the spatial form of some chemical waves. Here the constant v is the velocity of the wave while f is a continuously differentiable function defined on $(0, 1)$. Let $0 < \hat{q} < 1$ be a strictly monotonous solution of the boundary value problem such that

$$\lim_{\xi\to-\infty} \frac{\mathrm{d}\hat{q}}{\mathrm{d}\xi}(\xi) = \lim_{\xi\to\infty} \frac{\mathrm{d}\hat{q}}{\mathrm{d}\xi}(\xi) = 0, \tag{1.99}$$

and let $\hat{\xi}(q)$ be the value of the inverse of this solution.

(a) Show that the function $\hat{p}$ defined by

$$\hat{p}(q) = -\frac{\mathrm{d}\hat{q}}{\mathrm{d}\xi}(\hat{\xi}(q)) > 0$$

satisfies the boundary value problem

$$\hat{p}(q)\frac{\mathrm{d}\hat{p}}{\mathrm{d}q}(q) - v\hat{p}(q) + f(q) = 0, \tag{1.100}$$

$$\lim_{q\to 0} \hat{p}(q) = \lim_{q\to 1} \hat{p}(q) = 0 \tag{1.101}$$

on the interval $0 < q < 1$.

(b) In the case of $f(q) = q(1-q)(q-a)$; $0 < a < 1/2$ we speak of Nagumo equation, which is associated with the theoretical description of the propagations of electrical signals in living organisms [71].

On the basis of Eqn (1.100) determine the velocity v belonging to the function $\hat{p}$ defined by

$$\hat{p}(q) = \frac{1}{\sqrt{2}}q(1-q)$$

in the case of the Nagumo equation. Find the function $\hat{q}$ depending on ξ, too.

36. In the studies into the inner structures of the electrolyte solutions it is derived [3, p. 250] that the electrostatic potential of an ionic cloud around a given ion satisfies the equation

$$\Delta v = \kappa^2 v; \quad -\infty < x, y, z < \infty, \tag{1.102}$$

where

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

is the Laplacian and $\kappa > 0$ is a constant. A spherically symmetric solution of this equation is of the form $v(x, y, z) = f(r)$, where $r = \sqrt{x^2 + y^2 + z^2}$.

(a) Give the form of the Laplacian for spherically symmetric solutions. Use the quantity r defined previously.

(b) Using the result obtained in paragraph 36a determine a spherically symmetric solution of Eqn (1.102) for which $f(r) \to 0$ as $r \to \infty$.

1.6 OTHER PROBLEMS

1. In the Belousov–Zhabotinsky (BZ) reaction the bromate ions oxidize an organic substrate in a strongly acidic medium and bromination also takes place. On the surface of a not mixed BZ mixture placed in a Petri dish reaction fronts (chemical waves) of spiral form occur under appropriate conditions. Tyson and Keener [61] have given the equation of these spirals as

$$\mathbf{R}(r, t) = r\cos[\theta(r) - \omega t]\mathbf{i} + r\sin[\theta(r) - \omega t]\mathbf{j}, \tag{1.103}$$

where $\mathbf{R}(r, t)$ is a vector in the plane, $r \geq 0$ and $\omega > 0$ are parameters, $t \geq 0$ is time and θ a function to be determined by chemical considerations.

(a) As time t increases, the points of a spiral reaction front move, that is, the value of $\mathbf{R}$ belonging to a given parameter r changes. For a fixed value of r determine the velocity $\mathbf{v} = (\partial\mathbf{R}/\partial t)(r, t)$ of the motion, and the component $N(r, t)$ of the latter in the direction perpendicular to the vector $(\partial\mathbf{R}/\partial r)(r, t)$ ("normal velocity") [61].

(b) At a fixed value of t determine the curvature κ of the curve (1.103) on the basis of the formula

$$\kappa = \frac{X_r' Y_r'' - Y_r' X_r''}{[(X_r')^2 + (Y_r')^2]^{(3/2)}},$$

where X and Y are the components of the vector $\mathbf{R}$ in the usual rectangular coordinate system [61].

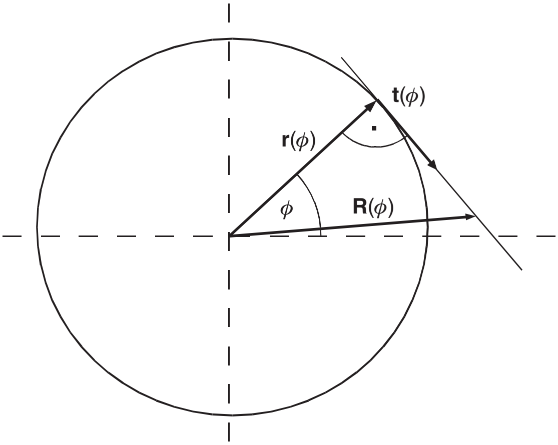


Figure 1.3 To the equation of the circle involute; $|\mathbf{r}(\phi)| = r_0$, $|\mathbf{t}(\phi)| = 1$

2. Tyson and Keener [61] have shown that the form of a spiral reaction front in problem 1 corresponds to an involute of a circle if one neglects the curvature effects. Lázár et al. [72] also described the BZ waves propagating in membrane rings by involutes of circles. According to a practical definition the curve described by the end point of a taut thread that is gradually unwound from a spool of the form of a circle (the radius of the spool is constant) is an involute of the circle. The notion of the involute can be extended to other objects as well [73].
   (a) On the basis of the definition above and Fig. 1.3 give an expression containing the parameter $\phi \geq 0$ for the vector $\mathbf{R}(\phi)$ whose end point describes an involute of the circle. Use r_0, $\mathbf{r}(\phi)$ and $\mathbf{t}(\phi)$.
   (b) Show that

$$\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}\phi}(\phi) \perp \mathbf{t}(\phi).$$

   (This property is also appropriate for the definition of an involute [73].)
   (c) Give the curve $\mathbf{R}(\phi)$ using rectangular coordinates. What is the distance between the points $\mathbf{R}(\phi_0)$ and $\mathbf{R}(\phi_0 + 2\pi)$?
3. We shall investigate the system of differential equations

$$\frac{\mathrm{d}x}{\mathrm{d}t}(t) = P(x(t), y(t)); \qquad \frac{\mathrm{d}y}{\mathrm{d}t}(t) = Q(x(t), y(t)), \tag{1.104}$$

where P and Q are continuously differentiable functions on an open set W of the plane. Such systems are frequently applied for the description of interacting populations in chemistry, biology, ecology, etc. [14, 74]. It can be shown [75, p. 162] that Eqn (1.104) has a solution for any initial point belonging to W. In the "kinematic" interpretation of Eqn (1.104) any solution (x, y) is represented by a curve depending on the parameter t, and the direction of the movement for increasing values of t is marked by an arrow on the curve. These curves are called trajectories.

(a) Prove Bendixson's criterion, which states the following: If the function

$$B = \frac{\partial P}{\partial x} + \frac{\partial Q}{\partial y}$$

is everywhere positive or everywhere negative on a rectangle T of W then T cannot contain a closed trajectory of Eqn (1.104). (Hint: apply Stokes' theorem to the function $\mathbf{v} = -Q\mathbf{i} + P\mathbf{j}$ using a closed trajectory C of Eqn (1.104).) Determine the integral

$$\oint_C (-Q\mathrm{d}x + P\mathrm{d}y),$$

and reach a contradiction. For a more general formulation of the criterion see [76, p. 212].)

(b) Consider the system of differential equations

$$\begin{aligned} \dot{x} &= a_1 + a_2x + a_3xy + a_4x^2 + a_5y^2, \\ \dot{y} &= b_1 + b_2y + b_3xy + b_4y^2 + b_5x^2 \end{aligned} \tag{1.105}$$

defined in the positive quadrant of the plane for which $a_1, b_1, a_5, b_5 \geq 0$ and $a_4, b_4 \leq 0$. On the basis of Bendixson's criterion what can be said about the signs of a_2, a_3, b_2 and b_3 if there exists a closed trajectory (a non-constant periodic solution) in the positive quadrant [77, 78]?

(c) Assume that the system of differential equations

$$\begin{aligned} \dot{x} &= \frac{a_1 + a_2x + a_3xy + a_4x^2 + a_5y^2}{xy}, \\ \dot{y} &= \frac{b_1 + b_2y + b_3xy + b_4y^2 + b_5x^2}{xy} \end{aligned} \tag{1.106}$$

is defined in the positive quadrant and its coefficients obey the conditions in paragraph 3b. Use Bendixson's criterion to prove that if Eqn (1.106) has a closed trajectory, it is of the form

$$\begin{aligned} \dot{x} &= a_2x + a_3xy, \\ \dot{y} &= b_2y + b_3xy. \end{aligned}$$

Table 1.5 The atomic orbitals $2p_x, 2p_y$ and $2p_z$ in hydrogenic atoms

Orbital	Wavefunction (ψ)
$2p_x$	$Nre^{-Zr/2a_0}\sin\theta\cos\phi$
$2p_y$	$Nre^{-Zr/2a_0}\sin\theta\sin\phi$
$2p_z$	$Nre^{-Zr/2a_0}\cos\theta$

r, θ, ϕ: spherical polar coordinates; Z: atomic number; a_0: Bohr radius

This problem is related to the uniqueness problem of the two-variable and at most second-order oscillators solved completely in [79].

4. In quantum mechanics the statistical interpretation of the wavefunction ψ requires the validity of the formula

$$\int |\psi|^2 \mathrm{d}V = 1 \tag{1.107}$$

("normed" wavefunction) [3, p. 297]. In Table 1.5 the wavefunctions of the atomic orbitals $2p_x$, $2p_y$ and $2p_z$ are collected. On the basis of Eqn (1.107) determine the factor N in the wavefunctions.

5. In quantum mechanics the prolate spheroidal coordinates [80] play a useful role. Let A and B be two points on the axis z at the coordinates $z=-(R/2)$ and $z=R/2$ and let C be a point with the coordinates (x, y, z). The prolate spheroidal coordinates ξ_1 and ξ_2 of the point C are defined by the formulas

$$\xi_1 = \frac{r_\mathrm{a}+r_\mathrm{b}}{R}; \qquad \xi_2 = \frac{r_\mathrm{a}-r_\mathrm{b}}{R}, \tag{1.108}$$

in which r_a and r_b are the distances $\overline{\mathrm{AC}}$ and $\overline{\mathrm{BC}}$, respectively. The third prolate spheroidal coordinate, ξ_3, agrees with the azimuthal angle ϕ of the spherical polar coordinate system. The coordinates (ξ_1, ξ_2, ξ_3) can vary in the intervals $\xi_1 \geq 1$, $-1 \leq \xi_2 \leq 1$ and $0 \leq \xi_3 < 2\pi$.

   (a) Give the relationships between the rectangular coordinates (x, y, z) and the prolate spheroidal coordinates (ξ_1, ξ_2, ξ_3) [80].

   (b) The Laplacian

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

   plays an important role in the theory of transport processes, classical and quantum mechanics, electrodynamics, etc. Determine its form in the coordinate system (ξ_1, ξ_2, ξ_3) [80]. Use the formulas

$$h_i = \sqrt{\left(\frac{\partial x}{\partial u_i}\right)^2 + \left(\frac{\partial y}{\partial u_i}\right)^2 + \left(\frac{\partial z}{\partial u_i}\right)^2}, \quad i = 1, 2, 3 \tag{1.109}$$

and

$$\begin{aligned}\Delta = \frac{1}{h_1 h_2 h_3}\left[\frac{\partial}{\partial u_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial}{\partial u_1}\right) + \frac{\partial}{\partial u_2}\left(\frac{h_1 h_3}{h_2}\frac{\partial}{\partial u_2}\right)\right.\\ \left. + \frac{\partial}{\partial u_3}\left(\frac{h_2 h_1}{h_3}\frac{\partial}{\partial u_3}\right)\right],\end{aligned} \tag{1.110}$$

where u_1, u_2 and u_3 are orthogonal curvilinear coordinates [81, 82]. Let $u_1 = \xi_1$, $u_2 = \xi_2$ and $u_3 = \xi_3$.

(c) In the LCAO description of the H_2^+ ion [3, p. 395] the overlap integral is

$$\int \psi_A \psi_B \, dV,$$

where

$$\psi_A(r_a) = \frac{1}{\sqrt{\pi a_0^3}} e^{-(r_a/a_0)}; \qquad \psi_B(r_b) = \frac{1}{\sqrt{\pi a_0^3}} e^{-(r_b/a_0)},$$

$a_0 > 0$ is the Bohr radius (a constant) and r_a and r_b are the distances of the electron from the nuclei A and B, respectively. Calculate this integral using the prolate spheroidal coordinates. Let the nuclei A and B be at the points A and B, respectively, so R will mean the nuclear distance. The volume element can be given by the curvilinear coordinates (u_1, u_2, u_3) as

$$dV = h_1 \, h_2 \, h_3 \, du_1 \, du_2 \, du_3, \tag{1.111}$$

where h_1, h_2 and h_3 are defined by Eqn (1.109) [83]. Let $u_1 = \xi_1$, $u_2 = \xi_2$ and $u_3 = \xi_3$.

6. According to thermodynamics any change of the internal energy of a substance depends only on the initial and the final states and is independent of the path of the change. A possible formula describing small changes in the internal energy U of a real gas is

$$dU = C_V \, dT + \frac{\alpha}{V^2} dV, \tag{1.112}$$

where $C_V > 0$ is the heat capacity of the gas (a constant), $\alpha > 0$ a constant characterizing the interactions between the gas particles, $T > 0$ the thermodynamical temperature and $V > 0$ the volume of the gas. The finite changes in the internal energy of the gas along the curve (path) C, are given by the line integral

$$\Delta U = \int_C C_V \, \mathrm{d}T + \frac{\alpha}{V^2} \mathrm{d}V.$$

Let the initial and the final points of C be (T_1, V_1) and (T_2, V_2), respectively $(T_1 \neq T_2)$. Calculate ΔU if the curve (path) C in a parametric form is

(a)

$$V = \frac{V_2 - V_1}{T_2 - T_1}\xi + \frac{V_1 T_2 - V_2 T_1}{T_2 - T_1}; \qquad T = \xi; \quad T_1 \le \xi \le T_2,$$

(b)

$$V = -\frac{V_2 - V_1}{T_2 - T_1}\xi + \frac{V_2 T_2 - V_1 T_1}{T_2 - T_1}; \qquad T = \frac{T_1 T_2}{\xi}; \quad T_1 \le \xi \le T_2.$$

Confirm that the results are in accordance with the statement in the first sentence of this problem.

7. Peptides are chain molecules consisting of amino acids linked by the peptide bond –CONH–. The amino acid units can join each other in an arbitrary order.

   (a) How many peptide molecules containing K amino acid units can be created from N different amino acids? Calculate the (approximate) numerical result when $N = 20$ and $K = 5, 20, 150$. Give a lower estimate of the full mass of these peptide molecules using the fact that K ^{12}C atom is definitely lighter than a peptide molecule.

   (b) Consider all the peptide molecules that consist of K amino acid units and are built from N different amino acids. How many molecules contain $L \le K$ of a given amino acid unit? Calculate the (approximate) numerical result for $N = 20, K = 150$ and $L = 30$.

   (The peptide molecules differ from each other in the order of the constituting amino acid units. The available quantity of the amino acids is unlimited and all the other practical problems can also be neglected.)

8. In the statistical description of an ensemble of particles we concentrate on the average properties rather than the individual particles themselves. It is an important question of Maxwell–Boltzmann statistics [3, p. 569] whether

how many ways exist for placing N distinguishable particles onto K energy levels such that there be $N_1, N_2, \dots, N_K$ particles on the levels labeled by $1, 2, \dots, K$, respectively. Assume that particle states of numbers $g_1, g_2, \dots, g_K$ are assigned to the energy levels $1, 2, \dots, K$, respectively. How many ways are there for the particles to populate these states? (Use a "pedestrian" model: particles → different things; energy level → drawer; state → a box in a drawer.)

9. In Bose–Einstein statistics [22, p. 201] we have $g_1, g_2, \dots, g_K$ particle states that belong to the energy levels labeled by $1, 2, \dots, K$, respectively. The number of the particles in a state is not limited, but the particles are assumed to be indistinguishable. In how many ways can the particles occupy these states if there must be $N_1, N_2, \dots, N_K$ particles on the energy levels $1, 2, \dots, K$, respectively? (Use a "pedestrian" model: particles → identical things; energy level → drawer; state → a box in a drawer.)
10. In Fermi–Dirac statistics [3, p. 420, 22, p. 201] we have $g_1, g_2, \dots, g_K$ particle states that belong to the energy levels labeled by $1, 2, \dots, K$, respectively. It is assumed that at most one particle can occupy a state and that the particles are indistinguishable. In how many ways can the particles occupy these states if there must be $N_1, N_2, \dots, N_K$ particles on the energy levels $1, 2, \dots, K$, respectively? (Use a "pedestrian" model: particles → identical things; energy level → drawer; state → a box in a drawer.)
11. The investigation of a one-dimensional chain molecule consisting of N monomers [3, p. 696] helps us to understand the spatial forms of the polymer molecules in different solutions. The monomers in this one-dimensional chain can rotate at the points where they are linked to each other, and when a monomer points forwards/backwards, the distance between the ends of the chain increases/decreases (see Fig. 1.4). We adopt the assumption that – in the

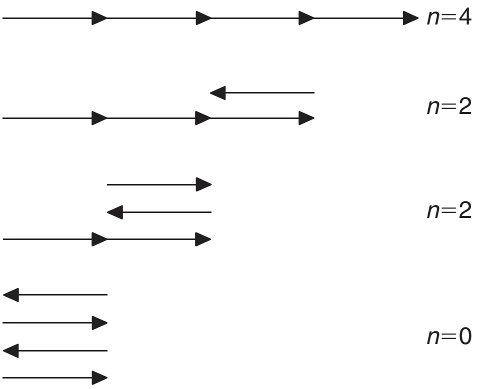


Figure 1.4 Several configurations of a linear polymer consisting of four monomers

lack of specific interactions – a monomer can point in both spatial directions with the probability $1/2$. We also assume that the chain molecule investigated lies on the axis x and one end of it is fixed at the origin.

(a) What is the probability $P(n,N)$ of the event that the free end of the chain molecule consisting of N monomers is at the coordinate n on the axis x (n is an integer since the unit we have chosen is the length of a monomer, and obviously $|n| \leq N$.)

(b) At what point of the axis x will the free end of the chain stay on average, that is, what is the average value of n? Is the latter equal to the square root of the average of n^2? Why?

(c) According to Stirling's formula [30, p. 588]

$$k! = k^k e^{-k+\theta/4k}\sqrt{2\pi k}; \quad 0 < \theta < 1,$$

where k is a positive integer. Using this formula show that for a fixed value of n

$$\lim_{i\to\infty} \frac{P(n,N_i)}{P_\mathrm{a}(n,N_i)} = 1,$$

where

$$P_\mathrm{a}(n,N_i) = \sqrt{\frac{2}{\pi}} \frac{N_i^{N_i}\sqrt{\frac{N_i}{N_i^2 - n^2}}}{2^{N_i}\left(\frac{N_i+n}{2}\right)^{\frac{N_i+n}{2}}\left(\frac{N_i-n}{2}\right)^{\frac{N_i-n}{2}}},$$

$N_i = |n| + 2i$ and $i = 1,2,3,\ldots$ (the subscript of P_a refers to the word "asymptotic"). Give the numeric values of $P_\mathrm{a}(0,N_i)$ and $P(0,N_i)$ for $N_i = 6, 10, 100$.

Chapter 2

Solutions

2.1 ALGEBRA

1. (a) Direct calculations show that the formula is valid. For example, for $n = 5$

$$H_6(x) = 8(8x^6 - 60x^4 + 90x^2 - 15)$$

and

$$\begin{aligned} 2xH_5(x) - 10H_4(x) &= 16x^2(4x^4 - 20x^2 + 15) \\ &\quad - 40(4x^4 - 12x^2 + 3) \\ &= 8(8x^6 - 60x^4 + 90x^2 - 15). \end{aligned}$$

(b) For even functions $f(x) = f(-x)$ and for odd ones $f(x) = -f(-x)$, where x is any element of the domain of definition. The polynomials containing only even and zero exponents are even functions while those containing only odd exponents are odd functions. Using this the investigated polynomials are even functions for $n = 0, 2, 4, 6, 8, 10$ and odd ones for $n = 1, 3, 5, 7, 9$.

(c) 0 is a zero for $n = 1, 3, 5, 7, 9$.

(d) For an arbitrarily chosen polynomial either $H_n(x) = H_n(-x)$ or $H_n(x) = -H_n(-x)$ is valid. Thus, $H_n(x) = 0$ always implies $H_n(-x) = 0$, that is, the real zeros are symmetrical to the origin in each case.

(e) Because of paragraph 1d the number of the real zeros is even if 0 is not a zero of the polynomial. Thus, an even number of zeros may occur for the cases $n = 2, 4, 6, 8, 10$. An equivalent starting point can be that a polynomial of even degree has an even number of zeros while a polynomial of odd degree has an odd number of zeros. Since the complex zeros of real polynomials – if they exist – always occur as conjugated pairs, only a polynomial of even degree can have an even number of real zeros. With this we obtain again at the previous result.

Table 2.1 Positive zeros of some Hermite polynomials on the basis of Descartes' rule of signs

n	2,3	4,5	6,7	8,9	10
Z	1	2,0	3,1	4,2,0	5,3,1

n: the degree of the Hermite-polynomial; Z: the possible number of the positive zeros.

(f) Descartes' rule of signs says that the number of the positive zeros of a polynomial is equal to the number of sign changes in the sequence of the coefficients of the polynomial or is smaller than that by an even number (the vanishing coefficients can be left out). The possible numbers of the positive zeros are collected in Table 2.1.

(g) i. $n = 1$

$$x = 0.$$

ii. $n = 2$

$$4x^2 - 2 = 0,$$
$$x_{1,2} = \pm\frac{\sqrt{2}}{2} = \pm 0.7071\ldots.$$

iii. $n = 3$

$$x = 0; \qquad 2x^2 - 3 = 0,$$
$$x_1 = 0; \qquad x_{2,3} = \pm\frac{\sqrt{6}}{2} = \pm 1.2247\ldots.$$

iv. $n = 4$

$$y = x^2,$$
$$4y^2 - 12y + 3 = 0,$$
$$y_{1,2} = \frac{12 \pm \sqrt{144 - 48}}{8} = \frac{3 \pm \sqrt{6}}{2},$$
$$x_{1,2} = \pm\sqrt{y_1} = \pm 1.6506\ldots$$

and

$$x_{3,4} = \pm\sqrt{y_2} = \pm 0.5246\ldots.$$

Table 2.2 Zeros of some Hermite polynomials

Degree	Zero
6	$\pm 0.4360\ldots$; $\pm 1.3358\ldots$; $\pm 2.3506\ldots$
7	0; $\pm 0.8162\ldots$; $\pm 1.6735\ldots$; $\pm 2.6519\ldots$
8	$\pm 0.3811\ldots$; $\pm 1.1571\ldots$; $\pm 1.9816\ldots$; $\pm 2.9306\ldots$
9	0; $\pm 0.7235\ldots$; $\pm 1.4685\ldots$; $\pm 2.2665\ldots$; $\pm 3.1909\ldots$
10	$\pm 0.3429\ldots$; $\pm 1.0366\ldots$; $\pm 1.7566\ldots$; $\pm 2.5327\ldots$; $\pm 3.4361\ldots$

v. $n=5$

$$\begin{aligned} x_1 &= 0, \\ y &= x^2, \\ 4y^2 - 20y + 15 &= 0, \\ y_{1,2} = \frac{20 \pm \sqrt{400-240}}{8} &= \frac{5 \pm \sqrt{10}}{2}, \\ x_{2,3} = \pm\sqrt{y_1} &= \pm 2.0201\ldots. \end{aligned}$$

and

$$x_{3,4} = \pm\sqrt{y_2} = \pm 0.9585\ldots.$$

(h) The numerically obtained results are summarized in Table 2.2.

2. (a) For an even function $f(x) = f(-x)$ while for an odd one $f(x) = -f(-x)$, where x is an arbitrary element of the domain of definition. The even functions are P_1^1, P_2^2 and P_{10}^2. The odd functions are P_3^2, P_5^2 and P_7^2.

(b) P_3^2, P_5^2 and P_7^2.

(c) For the functions in the table $P_l^m(x) = 0$ implies $P_l^m(-x) = 0$. Thus, the real zeros are symmetrical to the origin in each case.

(d) A function has an even number of real zeros if it does not vanish at 0 (cf. 2c).

(e) i.

$$P_2^2(x) = -3x^2 + 3,$$

the number of sign changes is 1 so the number of positive zeros also is 1.

ii.

$$P_3^2(x) = -15x^3 + 15x,$$

the number of sign changes is 1 so the number of positive zeros also is 1.

iii.

$$P_5^2(x) = \frac{1}{2}(-315x^5 + 420x^3 - 105x),$$

the number of sign changes is 2 so the number of positive zeros is 2 or 0.

iv.

$$P_7^2(x) = \frac{1}{8}(-9009x^7 + 15939x^5 - 7875x^3 + 945x),$$

the number of sign changes is 3 so the number of positive zeros is 3 or 1. Thus, a positive zero definitely exists.

v.

$$P_{10}^2(x) = -\frac{2078505}{128}x^{10} + \frac{5141565}{128}x^8 - \frac{2207205}{64}x^6 + \frac{765765}{64}x^4 - \frac{183645}{128}x^2 + \frac{3465}{128},$$

the number of sign changes is 5 so the number of positive zeros is 5, 3 or 1. Thus, a positive zero definitely exists.

(f) i. P_1^1: $x_{1,2} = \pm 1$.

ii. P_2^2: $x_{1,2} = \pm 1$.

iii. P_3^2: $x_1 = 0$; $x_{2,3} = \pm 1$.

iv. P_5^2: $x_1 = 0$; $x_{2,3} = \pm 1$; $x_{4,5} = \pm(\sqrt{3}/3) = \pm 0.5773\ldots$.

v. P_7^2: $x_1 = 0$; $x_{2,3} = \pm 1$;

$$y = x^2,$$

$$143y^2 - 110y + 15 = 0,$$

$$y_{1,2} = \frac{110 \pm \sqrt{110^2 - 4 \times 15 \times 143}}{2 \times 143},$$

$$x_{4,5} = \pm\sqrt{y_1} = \pm 0.7694\ldots; \quad x_{6,7} = \pm\sqrt{y_2} = \pm 0.4209\ldots.$$

(g) P_{10}^2: applying a numerical method to the polynomial in the second parentheses (see Table 1.2)

$$\begin{aligned} x_{1,2} &= \pm 0.1516\ldots; \quad x_{3,4} = \pm 1; \\ x_{5,6} &= \pm 0.4414\ldots; \quad x_{7,8} = \pm 0.6920\ldots; \\ x_{9,10} &= \pm 0.8814\ldots. \end{aligned}$$

3. (a) A negative root of $L_n^k(x)$ obviously is a positive root of $L_n^k(-x)$. Applying Descartes' rule of signs to the latter the number of sign changes is zero for each polynomial in the table. The number of the positive roots can be estimated as follows:
   - i. L_1^1: 1;
   - ii. L_2^1: 2 or 0;
   - iii. L_3^1: 3 or 1, so there exists at least 1 positive zero;
   - iv. L_4^1: 4, 2 or 0;
   - v. L_5^1: 5, 3, 2 or 0.

   (b) i. L_1^1: $x = 2$
   ii. L_2^1:

$$\begin{aligned} x^2 - 6x + 6 &= 0, \\ x_{1,2} &= \frac{6 \pm \sqrt{36-24}}{2} = 3 \pm \sqrt{3}, \\ x_1 &= 4.7320\ldots, \\ x_2 &= 1.2679\ldots. \end{aligned}$$

   (c) We must apply numerical methods.

   i. L_3^1:

$$x_1 = 0.9358\ldots; \quad x_2 = 3.3054\ldots; \\ x_3 = 7.7587\ldots.$$

   ii. L_4^1:

$$x_1 = 0.7432\ldots; \quad x_2 = 2.5716\ldots; \\ x_3 = 5.7311\ldots; \quad x_4 = 10.9538\ldots.$$

   iii. L_5^1:

$$x_1 = 0.6170\ldots; \quad x_2 = 2.1129\ldots; \\ x_3 = 4.6108\ldots; \quad x_4 = 8.3990\ldots; \\ x_5 = 14.2601\ldots.$$

4. (a) The sequence of signs of the coefficients in Eqn (1.1) is $\{+, +, -, -\}$, and this contains 1 sign change. This implies the existence of exactly one positive root.

(b) With the aid of numerical methods

$$10^6 \frac{[\mathrm{H}^+]}{c^\ominus} = 8.5420\ldots.$$

Using this $\mathrm{pH} = -\lg([\mathrm{H}^+]/c^\ominus) = 5.07\ldots$, which corresponds to a weakly acidic solution. On the uniqueness of roots in the equilibrium calculations see [84].

5.

$$\begin{aligned} k_1[\mathrm{X}]_\mathrm{s} - k_2[\mathrm{X}]_\mathrm{s}[\mathrm{Y}]_\mathrm{s} &= [\mathrm{X}]_\mathrm{s}\{k_1 - k_2[\mathrm{Y}]_\mathrm{s}\} = 0,\\ k_2[\mathrm{X}]_\mathrm{s}[\mathrm{Y}]_\mathrm{s} - k_3[\mathrm{Y}]_\mathrm{s} &= [\mathrm{Y}]_\mathrm{s}\{k_2[\mathrm{X}]_\mathrm{s} - k_3\} = 0, \end{aligned}$$

from which

$$[\mathrm{X}]_{\mathrm{s}1} = 0; \qquad [\mathrm{Y}]_{\mathrm{s}1} = 0$$

(trivial solution) and

$$[\mathrm{X}]_{\mathrm{s}2} = \frac{k_3}{k_2}; \qquad [\mathrm{Y}]_{\mathrm{s}2} = \frac{k_1}{k_2}.$$

6.

$$k_1' - k_2[\mathrm{X}]_\mathrm{s}[\mathrm{Y}]_\mathrm{s} = 0,$$

$$k_2[\mathrm{X}]_\mathrm{s}[\mathrm{Y}]_\mathrm{s} - k_3[\mathrm{Y}]_\mathrm{s} = [\mathrm{Y}]_\mathrm{s}\{k_2[\mathrm{X}]_\mathrm{s} - k_3\} = 0,$$

from which

$$[\mathrm{X}]_\mathrm{s} = \frac{k_3}{k_2}; \quad [\mathrm{Y}]_\mathrm{s} = \frac{k_1'}{k_3}.$$

7.

$$\begin{aligned} k_1[\mathrm{A}][\mathrm{X}]_\mathrm{s}^2 - k_2[\mathrm{X}]_\mathrm{s}[\mathrm{Y}]_\mathrm{s}^2 &= [\mathrm{X}]_\mathrm{s}\{k_1[\mathrm{A}][\mathrm{X}]_\mathrm{s} - k_2[\mathrm{Y}]_\mathrm{s}^2\} = 0,\\ k_2[\mathrm{X}]_\mathrm{s}[\mathrm{Y}]_\mathrm{s}^2 - k_3[\mathrm{Y}]_\mathrm{s} &= [\mathrm{Y}]_\mathrm{s}\{k_2[\mathrm{X}]_\mathrm{s}[\mathrm{Y}]_\mathrm{s} - \mathrm{k}_3\} = 0, \end{aligned}$$

from which

$$[\mathrm{X}]_{\mathrm{s}1} = 0; \qquad [\mathrm{Y}]_{\mathrm{s}1} = 0$$

and

$$[\mathrm{X}]_{\mathrm{s}2} = \frac{k_2}{k_1[\mathrm{A}]}\left(\frac{k_1k_3[\mathrm{A}]}{k_2^2}\right)^{2/3}; \qquad [\mathrm{Y}]_{\mathrm{s}2} = \left(\frac{k_1k_3[\mathrm{A}]}{k_2^2}\right)^{1/3}.$$

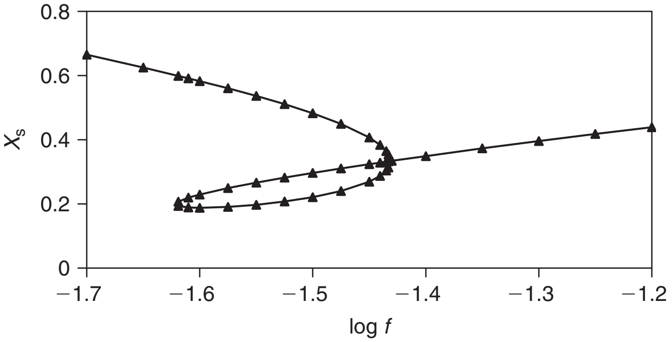


Figure 2.1 The solutions of Eqn (2.1); $f_2 = 1/135$; $y_0 = 10/27$ (Reprinted with modification from ref. [9], with permission from Elsevier)

8. (a) First we insert $k_2 = 1$ into the corresponding equations, which greatly simplifies the calculations. Then some algebraic manipulation yields for the solution (x_s, y_s) that

$$fx_s^3 - fx_s^2 + [f^2 + (f - f_2)y_0]x_s - f^2 = 0 \tag{2.1}$$

and

$$y_s = \frac{f(1 - x_s)}{x_s}.$$

Thus, to calculate x_s we must solve a cubic equation.

(b) To obtain Fig. 2.1 we have solved Eqn (2.1) numerically, and plotted the x_s values as required in the problem. According to the figure there are three distinct positive roots for appropriately fixed values of *f*. The curve in the figure resembles a pitchfork, and when such a situation occurs during the change of a parameter we usually speak of “pitchfork bifurcation”.

(c) Fig. 2.2 has been obtained by the numerical solution of Eqn (2.1). The engineering term “isola” refers to the existence of an isolated closed plane curve in the figure. According to the figure there are three distinct positive roots for appropriately fixed values of *f*.

(d) Fig. 2.3 has been obtained by the numerical solution of Eqn (2.1). The accepted name of this topology of roots is “mushroom”.

9. (a) Apart from a negative sign any of the four equations is the sum of the other three. Thus, we have only three independent equations for the determination of the four unknowns. For example, we may choose the last three equations and, with some calculation, we may express the unknowns x_s, z_s

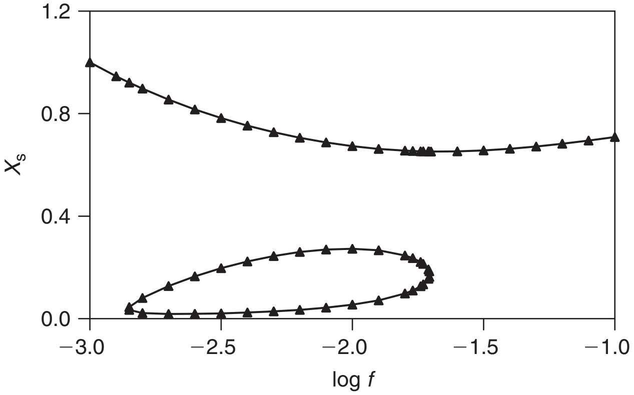


Figure 2.2 The solutions of Eqn (2.1); $f_2 = 0.001$; $y_0 = 0.25$ (Reprinted with modification from ref. [9], with permission from Elsevier)

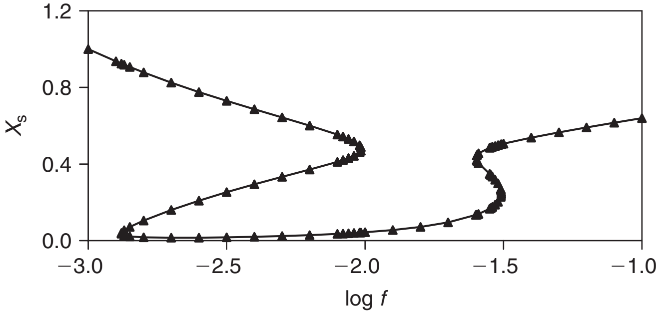


Figure 2.3 The solutions of Eqn (2.1); $f_2 = 0.001$; $y_0 = 0.29$ (Reprinted with modification from ref. [9], with permission from Elsevier)

and w_s with the aid of y_s. When $Y(y_s) \neq 0$

$$x_s(y_s) = \frac{k_2 y_s (k_7 y_s + k_4)(k_8 y_s + k_6)}{Y(y_s)},$$

$$z_s(y_s) = \frac{k_2 k_3 y_s (k_8 y_s + k_6)}{Y(y_s)}$$

and

$$w_s(y_s) = \frac{k_2 k_5 y_s (k_7 y_s + k_4)}{Y(y_s)},$$

where

$$Y(y_\mathrm{s}) = k_7k_8(k_1 + k_3 - k_5)y_\mathrm{s}^2 + [k_1(k_4k_8 + k_6k_7) + k_3k_6k_7 - k_4k_5k_8]\,y_\mathrm{s} + k_1k_4k_6.$$

Obviously, there are infinitely many y_s values for which $Y(y_\mathrm{s}) \neq 0$, and for any of these y_s values there exists a solution $\{x_\mathrm{s}(y_\mathrm{s}), y_\mathrm{s}, z_\mathrm{s}(y_\mathrm{s}), w_\mathrm{s}(y_\mathrm{s})\}$ of the original system of equations.

(b) With a somewhat lengthy but not difficult calculation we find that

$$c_1y_\mathrm{s}^3 + (c_2 - c_3b)y_\mathrm{s}^2 + (c_4 - c_5b)y_\mathrm{s} - c_6b = 0, \tag{2.2}$$

where

$$\begin{aligned} c_1 &= (k_1 + k_2 + k_3 - k_5)k_7k_8,\\ c_2 &= k_1(k_4k_8 + k_6k_7) + k_2(k_3k_8 + k_4k_8 + k_5k_7\\ &\quad + k_6k_7) + k_3k_6k_7 - k_4k_5k_8,\\ c_3 &= (k_1 + k_3 - k_5)k_7k_8,\\ c_4 &= k_1k_4k_6 + k_2(k_3k_6 + k_4k_5 + k_4k_6),\\ c_5 &= k_1(k_4k_8 + k_6k_7) + k_3k_6k_7 - k_4k_5k_8 \end{aligned}$$

and

$$c_6 = k_1k_4k_6.$$

(c) Substituting the data we find that $Y(y_\mathrm{s}) > 0$ for any y_s, moreover

$$\begin{aligned} &c_1 = 928; && c_2 = 107.2; && c_3 = 768.0;\\ &c_4 = 131.2; && c_5 = -276.8; && c_6 = 43.2. \end{aligned}$$

By the numerical solution of Eqn (2.2) we can construct Fig. 2.4. According to the figure there are three distinct positive roots for appropriately fixed values of b.

When b is changed continuously in Fig. 2.4, y_s changes smoothly along either the lower or the upper branches of the S shaped curve. There are, however, two values of b at which y_s leaves the branch along which it moved previously and jumps to the other one. The authors call these sudden changes “catastrophic” (cf. “catastrophe theory” [85]).

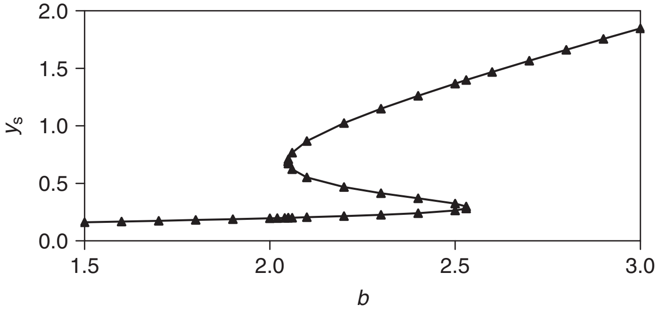


Figure 2.4 The solutions of Eqn (2.2); $k_1 = 1.8, k_2 = 1, k_3 = k_4 = k_7 = 8, k_5 = 5, k_6 = 3$ and $k_8 = 20$ (Reprinted with modification from ref. [10], (C) 2006 Oldenbourg Wissenschaftsverlag GmbH, with permission from Oldenbourg Wissenschaftsverlag GmbH)

10. (a) Using the given equations a simple calculation yields

$$\alpha_s^3 - 2(1+\beta_0)\alpha_s^2 + \left[(1+\beta_0)^2 + \left(1+\frac{\tau_{res}}{\tau_2}\right)^2 \frac{1}{\tau_{res}}\right]\alpha_s - \left(1+\frac{\tau_{res}}{\tau_2}\right)^2 \frac{1}{\tau_{res}} = 0 \tag{2.3}$$

and

$$\beta_s = \frac{1+\beta_0-\alpha_s}{1+(\tau_{res}/\tau_2)}.$$

On the left-hand side of Eqn (2.3) the sequence of the coefficients' signs is $\{+, -, +, -\}$, and this contains 3 sign changes. It follows from Descartes' rule of signs that the number of the positive roots is 1 or 3.

(b) i. Eqn (2.3) can be factorized as

$$(\alpha_s - 1)\left[\alpha_s^2 - \alpha_s + \left(1+\frac{\tau_{res}}{\tau_2}\right)^2 \frac{1}{\tau_{res}}\right] = 0,$$

from which

$$\alpha_{s1} = 1$$

and

$$\alpha_{s2,3} = \frac{1 \pm \sqrt{1 - 4\left(1+(\tau_{res}/\tau_2)\right)^2 \frac{1}{\tau_{res}}}}{2}. \tag{2.4}$$

For the last two roots we obtain two different positive values if and only if

$$1-4\left(1+\frac{\tau_{\mathrm{res}}}{\tau_2}\right)^2\frac{1}{\tau_{\mathrm{res}}}>0,$$

that is,

$$4\tau_{\mathrm{res}}^2+\tau_2(8-\tau_2)\tau_{\mathrm{res}}+4\tau_2^2<0 \tag{2.5}$$

is fulfilled. The left-hand side of Eqn (2.5) – if τ_2 is fixed and τ_{res} is changed – is a parabola standing upwards. This has a negative part if and only if the equation

$$4\tau_{\mathrm{res}}^2+\tau_2(8-\tau_2)\tau_{\mathrm{res}}+4\tau_2^2=0$$

has two distinct real roots. By virtue of

$$\tau_{\mathrm{res}1,2}=\frac{-\tau_2(8-\tau_2)\pm\sqrt{\tau_2^2(8-\tau_2)^2-64\tau_2^2}}{8} \tag{2.6}$$

this occurs if and only if

$$\tau_2^2(8-\tau_2)^2-64\tau_2^2>0,$$

that is,

$$\tau_2>16.$$

In this case the roots are not only real but $\tau_{\mathrm{res}1,2}>0$ is also valid. Thus, Eqn (2.3) will have three distinct positive roots in the positive interval $(\tau_{\mathrm{res}2},\tau_{\mathrm{res}1})$ for $\tau_2>16$.

ii. If $\tau_2=20$, Eqn (2.6) yields $\tau_{\mathrm{res}2}=30-10\sqrt{5}=7.6393\ldots$ and $\tau_{\mathrm{res}1}=30+10\sqrt{5}=52.3606\ldots$. Fig. 2.5 has been constructed by the aid of Eqn (2.4). A similar "isola" can be seen in Fig. 2.2.

11. From the given equations

$$\mathrm{Tr}=k_1+2k_3x_{\mathrm{s}}+k_4y_{\mathrm{s}}+c_1+2c_3y_{\mathrm{s}}+c_4x_{\mathrm{s}},$$

which – taking into account Eqn (1.5) and the signs of the coefficients – leads to the expression

$$\mathrm{Tr}=-\frac{(k_0+k_2y_{\mathrm{s}}+k_5y_{\mathrm{s}}^2)}{x_{\mathrm{s}}}+k_3x_{\mathrm{s}}-\frac{(c_0+c_2x_{\mathrm{s}}+c_5x_{\mathrm{s}}^2)}{y_{\mathrm{s}}}+c_3y_{\mathrm{s}}\leq 0. \tag{2.7}$$

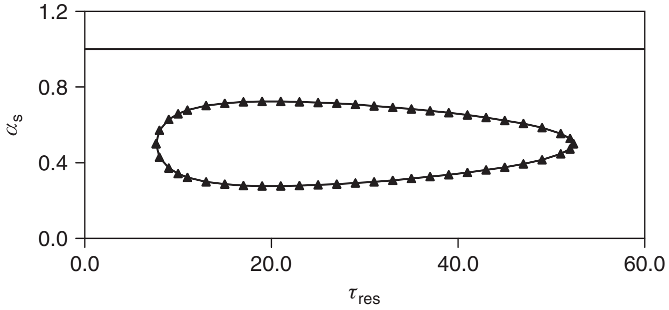


Figure 2.5 The solutions of Eqn (2.3); $\tau_2 = 20$; $\beta_0 = 0$ (Reprinted with modification from ref. [11], with permission from Elsevier)

Employing the quadratic formula we obtain

$$\lambda_{1,2} = \frac{\mathrm{Tr} \pm \sqrt{\mathrm{Tr}^2 - 4\Delta}}{2}. \tag{2.8}$$

(a) Using Eqn (2.8) we find that $\Delta > 0$ and

$$\lambda_{1,2} < 0.$$

(b) Using Eqn (2.8) we find that $\mathrm{Tr}^2 - 4\Delta < 0$ and, because of Eqn (2.7),

$$\mathrm{Re}(\lambda_{1,2}) = \mathrm{Tr} < 0.$$

(c) Since all the terms of Eqn (2.7) are non-negative,

$$\mathrm{Re}(\lambda_{1,2}) = \mathrm{Tr} = 0$$

is satisfied if and only if

$$k_0 = k_2 = k_3 = k_5 = 0$$

and

$$c_0 = c_2 = c_3 = c_5 = 0.$$

The assertion immediately follows from this.

12. (a) After simple algebraic manipulations $x_s = y_s = z_s = 0$ and for $1 + x_s \neq 0$

$$x_s = \frac{(1 - f - q) \pm \sqrt{(1 - f - q)^2 + 4q(1 + f)}}{2q}, \tag{2.9}$$

$$y_s = \frac{fx_s}{1+x_s} = \frac{1}{2}(1+f-qx_s) \tag{2.10}$$

and

$$z_s = x_s. \tag{2.11}$$

For the positive solution we choose the plus sign Eqn (2.9).

(b) i. The relation $\alpha > 0$ is definitely valid if $y_s + 2qx_s - 1 > 0$. To prove the latter we start with the following transformation:

$$y_s + 2qx_s - 1 = 2y_s + 2qx_s - 1 - y_s.$$

Using Eqn (2.10) twice we first obtain

$$2y_s + 2qx_s - 1 - y_s = f + qx_s - y_s$$

and then

$$f + qx_s - y_s = \frac{f + qx_s + qx_s^2}{1+x_s} > 0.$$

It follows from $\alpha > 0$ that $A(w) > 0$. Employing Eqn (2.9) we find that

$$2qx_s + q - 1 + f = \sqrt{(1-f-q)^2 + 4q(1+f)} > 0,$$

which implies $C(w) > 0$.

ii. Let a, b and c be real numbers and let $b > 0$. If $c = ab$, the general equation

$$\lambda^3 + a\lambda^2 + b\lambda + c = 0 \tag{2.12}$$

can be factorized as

$$(\lambda + a)(\lambda + i\sqrt{b})(\lambda - i\sqrt{b}) = 0,$$

that is, one root of the equation is real and the other two are imaginary. Conversely, if a cubic equation has the roots $\lambda_1 = -a$ and $\lambda_{2,3} = \pm i\sqrt{b}$ $(b > 0)$ then, apart from a constant multiplier, the equation can be written as

$$(\lambda + a)(\lambda + i\sqrt{b})(\lambda - i\sqrt{b}) = 0,$$

which yields Eqn (2.12) with $c = ab$. (We have used that for real polynomial equations, the complex roots always occur in conjugate pairs.) For Eqn (1.8) it is sufficient to show that the equation $A(w_s)B(w_s) = C(w_s)$ has a unique positive solution. Using the formulas of $A(w), B(w)$ and $C(w)$ the equation to be solved is

$$\alpha w_s^2 + [\alpha^2 + f(1 - x_s)]w_s + \alpha[2qx_s^2 + x_s(q - 1) + f] = 0,$$

where the constant term is negative by condition. Thus, according to Descartes' rule of signs, the equation has exactly one positive root.

13. Evidently, the roots of $j_0(x) = 0$ are the same as those of $\sin x = 0$, so these roots can be found simply. In the other cases we can obtain rough initial values for the roots by the following theorem: if f is a continuous function and $f(a) f(b) < 0$ then $f(\xi) = 0$ for some $a < \xi < b$. A The final values of the roots have been collected in Table 2.3.
14. If f is a continuous function and $f(a)f(b) < 0$ then $f(\xi) = 0$ for some $a < \xi < b$. This well-known theorem helps us to estimate the roots. The final results are: 5.0277 ...; 7.3349 ...; 11.3812 ...; 13.6543 ...; 17.6837 ...; 19.9511 ...; 23.9760 ... and 26.2414 ....
15. (a) Some calculation yields

$$a_0x^3 + a_1x^2 + a_2x + a_3 = 0, \tag{2.13}$$

where

$$a_0 = 4n(\mathrm{CO})^2(K_x + 1),$$
$$a_1 = -4n(\mathrm{CO})(K_x + 1)[n(\mathrm{CO}) + n(\mathrm{H_2})],$$
$$a_2 = K_x n(\mathrm{H_2})[4n(\mathrm{CO}) + n(\mathrm{H_2})] + [n(\mathrm{CO}) + n(\mathrm{H_2})]^2$$

and

$$a_3 = -K_x n(\mathrm{H_2})^2.$$

Table 2.3 Some zeros of the spherical Bessel functions of the first kind

	Zeros			
j_0	π	2π	3π	4π
j_1	4.4934...	7.7252...	10.9041...	
j_2	5.7634...	9.0950...	12.3229...	
j_3	6.9879...	10.4171...	13.6980...	

The sequence of signs of the coefficients is $\{+, -, +, -\}$ for any positive values of the parameters. According to Descartes' rule of signs the 3 sign changes imply 1 or 3 roots for any positive values of the parameters.

(b) If f is a continuous function and $f(a)f(b) < 0$ then $f(\xi) = 0$ for some $a < \xi < b$. This well-known theorem helps us to estimate the roots where necessary. The roots for which the denominator of Eqn (1.10) is not zero will satisfy Eqn (1.10). To have a chemical meaning a root must obey the relations $x < 1$ and $n(\mathrm{H_2}) - 2xn(\mathrm{CO}) > 0$.

i. With $n(\mathrm{CO}) = n(\mathrm{H_2}) = 1\,\mathrm{mol}$ Eqn (2.13) becomes

$$4(K_x + 1)x^3 - 8(K_x + 1)x^2 + (5K_x + 4)x - K_x = 0.$$

We notice that $x_1 = 1$ and so the equation can be factorized as

$$(x - 1)[4(K_x + 1)x^2 - 4(K_x + 1)x + K_x] = 0.$$

From the vanishment of the quadratic factor

$$x_2 = \frac{\sqrt{K_x + 1} - 1}{2\sqrt{K_x + 1}} \quad \text{and} \quad x_3 = \frac{\sqrt{K_x + 1} + 1}{2\sqrt{K_x + 1}}.$$

With $K_x = 2.1$ we have

$$x_2 = 0.2160\ldots \quad \text{and} \quad x_3 = 0.7839\ldots.$$

The only solution that has a chemical meaning is x_2.

ii. With $n(\mathrm{CO}) = 1\,\mathrm{mol}$, $n(\mathrm{H_2}) = 2$ mol and $K_x = 2.1$ Eqn (2.13) becomes

$$f(x) = 12.4x^3 - 37.2x^2 + 34.2x - 8.4 = 0.$$

On the basis of our estimates we conjecture that there is only one root in the interval $[0, 1]$. Using numerical methods we obtain

$$x = 0.3885\ldots.$$

iii. With $n(\mathrm{CO}) = 3\,\mathrm{mol}$, $n(\mathrm{H_2}) = 1\,\mathrm{mol}$ and $K_x = 2.1$ Eqn (2.13) becomes

$$f(x) = 334.8x^3 - 446.4x^2 + 129.9x - 6.3 = 0.$$

Using appropriate software

$$x_1 = 0.0605\ldots,$$
$$x_2 = 0.3297\ldots$$

and

$$x_3 = 0.9430\ldots,$$

but x_1 is the only root that has a chemical meaning.

Conjecture: from all the possible ratios $n(\mathrm{CO}) : n(\mathrm{H_2})$ it is the ratio 1:2 (the stoichiometric ratio) that maximizes the equilibrium conversion x.

16. (a) Some calculation yields

$$a_0x^4 + a_1x^3 + a_2x^2 + a_3x + a_4 = 0, \tag{2.14}$$

where

$$\begin{aligned}
a_0 &= n(\mathrm{N_2})^3(27K_x - 16),\\
a_1 &= n(\mathrm{N_2})^2[n(\mathrm{H_2}) + n(\mathrm{N_2})](16 - 27K_x),\\
a_2 &= n(\mathrm{N_2})\{9K_xn(\mathrm{H_2})[n(\mathrm{H_2}) + 3n(\mathrm{N_2})]\\
&\quad - 4[n(\mathrm{H_2}) + n(\mathrm{N_2})]^2\},\\
a_3 &= -K_xn(\mathrm{H_2})^2[n(\mathrm{H_2}) + 9n(\mathrm{N_2})]
\end{aligned}$$

and

$$a_4 = K_xn(\mathrm{H_2})^3.$$

For the chemically meaningful, that is, positive values of the parameters the possible sign sequences of the coefficients are

$$\{+, -, \pm, -, +\}$$

and

$$\{-, +, \pm, -, +\}.$$

In the first case the number of the positive roots is 4, 2 or 0, while in the second it is 3 or 1.

(b) If f is a continuous function and $f(a)f(b) < 0$ then $f(\xi) = 0$ for some $a < \xi < b$. This well-known theorem helps us to estimate the roots where necessary. For the roots of the original equation $x \neq 1$ and $n(H_2) - 3xn(N_2) \neq 0$ must be valid. The chemically meaningful roots obey the relations $x < 1$ and $n(H_2) - 3xn(N_2) > 0$.

i. Substituting the given amounts of matter into Eqn (2.14) we obtain

$$(27K_x - 16)x^4 - 2(27K_x - 16)x^3 + (36K_x - 16)x^2 - 10K_x x + K_x = 0.$$

We notice that $x_1 = 1$ is a root of this equation, so we can write that

$$(x - 1)[(27K_x - 16)x^3 - (27K_x - 16)x^2 + 9K_x x - K_x] = 0.$$

Thus, the other three roots can be calculated from a cubic equation. Using the given value of K_x the vanishment of the second factor leads to

$$1190.9x^3 - 1190.9x^2 + 402.3x - 44.7 = 0.$$

By the help of appropriate software we find the root

$$x_2 = 0.2483\ldots$$

in the interval (0, 1). The root is chemically meaningful.

ii. In this case we can take the square roots of both sides of Eqn (1.11), or, in other words, the left-hand side of Eqn (2.14) can be written as a product of two quadratic factors provided $27K_x - 16 \neq 0$. Thus, the solution of the quartic equation can now be reduced to the solutions of the quadratic equations

$$x^2 - 2x + \frac{3\sqrt{3K_x}}{3\sqrt{3K_x} + 4} = 0$$

and

$$x^2 - 2x + \frac{3\sqrt{3K_x}}{3\sqrt{3K_x} - 4} = 0.$$

For the given value of K_x it is easy to see that the first equation yields the root

$$x_1 = 0.6786\ldots.$$

in the interval [0,1] while the second equation has two conjugated complex roots. The root x_1 is chemically meaningful.

iii. With the substitution of the parameter values into Eqn (2.14) the equation to be solved is

$$\begin{aligned}f(x) = 32154.3x^4 - 42872.4x^3 \\ +11877x^2 - 1251.6x + 44.7 = 0.\end{aligned}$$

Some preliminary estimates show that there may be two roots in the interval $[0, 1]$ but a numerical procedure shows that $x_1 = 0.0795\ldots$ and $x_2 = 1.0021\ldots$. The root x_1 is chemically meaningful.

17. (a) After a somewhat lengthy but not difficult calculation we obtain

$$x^3 - 3x^2 - 3x - 1 = 0. \tag{2.15}$$

(b) In Eqn (2.15) the sequence of signs of the coefficients is $\{+, -, -, -\}$, which contains 1 sign change. Because of the Descartes' rule of signs the number of the positive roots is 1. In this case it is worth solving the cubic equation exactly. Using the appropriate formulas

$$x = 2^{2/3} + 2^{1/3} + 1. \tag{2.16}$$

(c) A direct calculation on the basis of Eqns (1.12) and (1.14) yields

$$T_{\mathrm{c}}^{3/2} = \frac{a(x-1)^2(2x+1)}{bRx^2(x+1)^2}.$$

If we insert Eqn (2.16) into this equation but leave x^2 in the denominator we arrive at the desired expression:

$$T_{\mathrm{c}} = \left(\frac{3a}{bRx^2}\right)^{2/3}. \tag{2.17}$$

A combination of Eqns (1.14), (2.15), (2.17) and (1.15) leads to

$$p_{\mathrm{c}} = \left(\frac{a^2R}{3b^5x^7}\right)^{1/3}. \tag{2.18}$$

(d) Using Eqns (1.14), (2.17) and (2.18)

$$Z_c = \frac{p_c V_{mc}}{RT_c} = \frac{1}{3}.$$

Epstein [19] notes that the value $(1/Z_c) = 3$ is already higher than $(1/Z_c) = (8/3) = 2.666\ldots$ computed from the van der Waals equation, but still remains well below the average of the $1/Z_c$ values measured for the apolar and "non-quantum" gases. Some equations of state predict $1/Z_c$ values that are even more close to the experimental ones.

18. (a)

$$pV^3 - n(RT + bp)V^2 + an^2V - abn^3 = 0.$$

(b) The sequence of sign changes is $\{+, -, +, -\}$, the number of sign changes is 3, so – according to Descartes' rule of signs – the number of the positive roots is 1 or 3.

(c) On the basis of chemical considerations the needed root must be reasonably close to the value

$$V_0 = \frac{nRT}{p} = 2.4775\ldots \times 10^{-3}\,\mathrm{m}^3.$$

Using the latter as an initial value a numerical procedure yields

$$V = 2.4596\ldots \times 10^{-3}\,\mathrm{m}^3$$

for the root of the cubic equation. By appropriate mathematical software it is easy to see that for the present values of the parameters there is only one positive real root, the other two roots are complex.

19. If f is a continuous function and $f(a)f(b) < 0$ then $f(\xi) = 0$ for some $a < \xi < b$. Using this theorem we can estimate the root of the equation

$$0.841x - 0.314x \log x - 18 = 0,$$

where $x = T/\mathrm{K}$. Using appropriate software

$$x = 312.5678\ldots.$$

20. For the cases of AgCl and AgI we must solve the equations

$$1.0 \times 10^{-10} = x^2 10^{-2\times 0.509\sqrt{x+0.0001}} \tag{2.19}$$

and

$$1.0 \times 10^{-16} = x^2 10^{-2\times 0.509\sqrt{x+0.0001}}, \qquad (2.20)$$

respectively, where

$$x = \frac{S}{m^{\ominus}}.$$

(a) For AgCl the substitution $x = 0$ under the radical sign gives the equation

$$1.0 \times 10^{-10} = x^2 10^{-2\times 0.509\sqrt{0.0001}},$$

whose positive root is

$$x_1 = 1.0117\ldots \times 10^{-5}.$$

In the case of AgI the substitution $x = 0$ under the radical sign leads to

$$1.0 \times 10^{-16} = x^2 10^{-2\times 0.509\sqrt{0.0001}},$$

and the positive root is now

$$x_1 = 1.0117\ldots \times 10^{-8}.$$

(b) Two positive roots of Eqn (2.19) revealed by mathematical/spreadsheet software are

$$x_1 = 1.0123\ldots \times 10^{-5}; \qquad x_2 = 206.5341\ldots,$$

and those of Eqn (2.20) are

$$x_1 = 1.0117\ldots \times 10^{-8}; \qquad x_2 = 437.0059\ldots.$$

Thus, the x_1 values obtained from the simplified and the original equations are close to each other, but we remark that they are not exactly the same even in the case of AgI. The x_2 roots of the original equations are chemically irrelevant.

21. If f is a continuous function and $f(a)f(b) < 0$ then $f(\xi) = 0$ for some $a < \xi < b$. Using this well-known theorem the root can be roughly estimated, and an appropriate numerical procedure yields

$$d = 2.4928\ldots.$$

Thus, $R_{\mathrm{AB}} \approx 132\,\mathrm{pm}$, which cannot be considered a good approximation from a physical point of view since the exact equilibrium bond distance of

H_2^+ is 106 pm [23, p. 223]. Other – more sophisticated – methods give more accurate results.

2.2 LINEAR ALGEBRA

1. The solutions of the linear systems of equations are given as row matrices (row vectors). In a row matrix the unknowns are expressed by some arbitrarily changeable parameters. In each row matrix the first, second, etc. matrix elements respectively, correspond to the first, second, etc. stoichometric coefficients of the associated reaction equation counted from the left. The electric charge is denoted by q.

(a)
$$\begin{array}{lrcl} \mathrm{H}: & 2x & = & 2z \\ \mathrm{O}: & 2y & = & z \end{array}$$
$$(\,2c \quad c \quad 2c\,)$$

(b)
$$\begin{array}{lrcl} \mathrm{Ca}: & x & = & z+u \\ \mathrm{O}: & 2x & = & 3u+v \\ \mathrm{H}: & 2x & = & 2v \\ \mathrm{S}: & 2y & = & 5z+2u \end{array}$$
$$(\,3c \quad 6c \quad 2c \quad c \quad 3c\,)$$

(c)
$$\begin{array}{lrcl} \mathrm{S}: & x & = & u \\ \mathrm{O}: & 2y+z & = & 4u \\ \mathrm{H}: & 2z & = & 2u \end{array}$$
$$(\,2c \quad 3c \quad 2c \quad 2c\,)$$

(d)
$$\begin{array}{lrcl} \mathrm{H}: & x & = & 2u \\ \mathrm{Cl}: & x & = & 2z+2v \\ \mathrm{Mn}: & y & = & z \\ \mathrm{O}: & 2y & = & u \end{array}$$
$$(\,4c \quad c \quad c \quad 2c \quad c\,)$$

(e)
$$\begin{array}{lrcl} \mathrm{K}: & x & = & z \\ \mathrm{Mn}: & x & = & u \\ \mathrm{O}: & 4x & = & v \\ \mathrm{H}: & y & = & 2v \\ \mathrm{Cl}: & y & = & z+2u+2w \end{array}$$
$$(\,2c \quad 16c \quad 2c \quad 2c \quad 8c \quad 5c\,)$$

(f)
$$\begin{array}{lrcl}
\mathrm{K}: & 2x & = & z \\
\mathrm{Cr}: & 2x & = & u \\
\mathrm{O}: & 7x & = & v \\
\mathrm{H}: & y & = & 2v \\
\mathrm{Cl}: & y & = & z+3u+2w
\end{array}$$
$$(c \quad 14c \quad 2c \quad 2c \quad 7c \quad 3c)$$

(g)
$$\begin{array}{lrcl}
\mathrm{Br}: & x & = & 2u \\
\mathrm{Mn}: & y & = & v \\
\mathrm{O}: & 2y & = & w \\
\mathrm{H}: & z & = & 2w \\
q: & z-x & = & 2v
\end{array}$$
$$(2c \quad c \quad 4c \quad c \quad c \quad 2c)$$

(h)
$$\begin{array}{lrcl}
\mathrm{Br}: & x & = & 2u \\
\mathrm{Cl}: & 2y & = & z \\
q: & -x & = & -z
\end{array}$$
$$(2c \quad c \quad 2c \quad c)$$

(i)
$$\begin{array}{lrcl}
\mathrm{I}: & x+y & = & 2u \\
\mathrm{O}: & 3x & = & v \\
\mathrm{H}: & z & = & 2v \\
q: & z-x-y & = & 0
\end{array}$$
$$(c \quad 5c \quad 6c \quad 3c \quad 3c)$$

(j)
$$\begin{array}{lrcl}
\mathrm{K}: & x & = & 2v \\
\mathrm{Mn}: & x & = & u \\
\mathrm{O}: & 4x+4y+2z & = & 4u+4v+w+2r \\
\mathrm{S}: & y & = & v+u \\
\mathrm{H}: & 2y+2z & = & 2w
\end{array}$$
$$(4c_1 \quad 6c_1 \quad 4c_2 \quad 4c_1 \quad 2c_1 \quad 6c_1+4c_2 \quad 5c_1+2c_2)\,.$$

Notice that in the case 1j two parameters (c_1 and c_2) can be chosen freely (see also [86]). This is very rare for reaction equations that describe real chemical processes. If we restrict ourselves to solutions consisting of integers, the equations above are called Diophantine equations [86].

2. The rank of the stoichiometric matrix is denoted by ρ.

(a) $\begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix}; \qquad \rho = 1$

(b) $$\begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 1 & 1 \\ 0 & 1 \end{pmatrix}; \qquad \rho = 2$$

(c) $$\begin{pmatrix} -1 & 1 & 0 & -1 \\ 1 & -1 & 0 & 3 \\ 1 & -1 & -1 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & -1 \end{pmatrix}; \qquad \rho = 3$$

(d) $$\begin{pmatrix} -1 & 0 & -1 & 0 & 1 \\ 2 & -1 & 1 & 1 & -2 \\ 0 & -1 & 0 & 1 & 0 \\ 0 & 1 & 1 & -1 & 0 \\ 0 & 1 & -1 & -1 & 0 \end{pmatrix}; \qquad \rho = 3$$

(e) $$\begin{pmatrix} -1 & 1 & 0 & 0 & -1 & 1 \\ 2 & -2 & -1 & 1 & 1 & -1 \\ 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & -1 & -1 & 1 \\ 0 & 0 & 0 & 0 & 1 & -1 \end{pmatrix}; \qquad \rho = 3$$

(f) $$\begin{pmatrix} -1 & 1 & 1 \\ -1 & 1 & 0 \\ 1 & -1 & -1 \\ 0 & 0 & 1 \end{pmatrix}; \qquad \rho = 2$$

(g) $$\begin{pmatrix} -1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \\ 0 & 0 & 1 \end{pmatrix}; \qquad \rho = 3$$

3. Let the number of the substances and the reactions be N and R, respectively. If necessary, renumber the substances as follows:

   - The substances taking part in the 1st reaction obtain the numbers $1, 2, \ldots, n_1$.
   - For $j = 2, \ldots, R$ the substances that first appear in the jth reaction obtain the numbers $n_{j-1}+1, n_{j-1}+2, \ldots, n_{j-1}+n_j$. Evidently, $n_1 + n_2 + \cdots + n_R = N$.

The linear independence of the columns of the stoichiometric matrix – that is, the linear independence of the reactions – is determined by the system of equations

$$\sum_{j=1}^{R} \nu_{ij} c_j = 0; \qquad i = 1, 2, \dots, N, \tag{2.21}$$

which contains the elements of the stoichiometric matrix and the unknowns $c_1, c_2, \dots, c_R$. In the case of a stoichiometric matrix obtained by the previous renumbering we obtain $c_R = 0, c_{R-1} = 0, \dots, c_2 = 0$ from the groups containing $n_R, n_{R-1}, \dots, n_2$ equations as we proceed upwards in Eqn (2.21). This is because of the vanishment of the corresponding elements of the stoichiometric matrix: in the first group of equations there are no other unknowns before c_R; in the second group of equations there are no other unknowns before c_{R-1}, and there are only vanishing unknowns behind it, etc. Finally, from the uppermost group containing n_1 equations we find $c_1 = 0$.

Since all the coefficients c_j vanish, the columns of the stoichiometric matrix – that is, the reactions – are linearly independent. Thus, the rank of the stoichiometric matrix is equal to the number R of the reactions.

4. Let q denote the electric charge and let ρ be the rank of the formula matrix. First we give the formula matrices of the systems in problem 2:

$$\text{(a)}\quad \begin{array}{cccc} & (1) & (2) & (3) \\ \mathrm{H} & 2 & 0 & 2 \\ \mathrm{O} & 0 & 2 & 2 \end{array}; \qquad \rho = 2$$

$$\text{(b)}\quad \begin{array}{ccccc} & (1) & (2) & (3) & (4) \\ \mathrm{H} & 2 & 1 & 1 & 0 \\ \mathrm{O} & 3 & 3 & 0 & 3 \\ \mathrm{C} & 1 & 1 & 0 & 1 \\ q & 0 & -1 & 1 & -2 \end{array}; \qquad \rho = 2$$

$$\text{(c)}\quad \begin{array}{cccccc} & (1) & (2) & (3) & (4) & (5) \\ \mathrm{N} & 2 & 1 & 1 & 0 & 1 \\ \mathrm{O} & 5 & 2 & 3 & 2 & 1 \end{array}; \qquad \rho = 2$$

$$\text{(d)}\quad \begin{array}{cccccc} & (1) & (2) & (3) & (4) & (5) \\ \mathrm{H} & 0 & 0 & 2 & 1 & 1 \\ \mathrm{Br} & 2 & 1 & 0 & 1 & 0 \end{array}; \qquad \rho = 2$$

$$\text{(e)}\quad \begin{array}{cccccc} & (1) & (2) & (3) & (4) & (5) \\ \mathrm{C} & 0 & 0 & 1 & 1 & 1 \\ \mathrm{O} & 0 & 0 & 1 & 1 & 1 \\ \mathrm{Cl} & 2 & 1 & 0 & 1 & 2 \end{array}; \qquad \rho = 2$$

The formula matrices of systems in the present problem are as follows:

$$\text{(a)}\quad \begin{array}{ccccccc} & \mathrm{CaC_2O_4} & \mathrm{Ca^{2+}} & \mathrm{C_2O_4^{2-}} & \mathrm{HC_2O_4^{-}} & \mathrm{H_2C_2O_4} & \mathrm{H^+} \\ \mathrm{H} & 0 & 0 & 0 & 1 & 2 & 1 \\ \mathrm{Ca} & 1 & 1 & 0 & 0 & 0 & 0 \\ \mathrm{C} & 2 & 0 & 2 & 2 & 2 & 0 \\ \mathrm{O} & 4 & 0 & 4 & 4 & 4 & 0 \\ q & 0 & 2 & -2 & -1 & 0 & 1 \end{array}; \quad \rho = 3$$

$$\text{(b)}\quad \begin{array}{ccccccc} & \mathrm{Na_3PO_4} & \mathrm{Na_2HPO_4} & \mathrm{NaH_2PO_4} & \mathrm{H_3PO_4} & \mathrm{NaOH} & \mathrm{H_2O} \\ \mathrm{H} & 0 & 1 & 2 & 3 & 1 & 2 \\ \mathrm{Na} & 3 & 2 & 1 & 0 & 1 & 0 \\ \mathrm{O} & 4 & 4 & 4 & 4 & 1 & 1 \\ \mathrm{P} & 1 & 1 & 1 & 1 & 0 & 0 \end{array}; \quad \rho = 3$$

$$\text{(c)}\quad \begin{array}{cccccc} & \mathrm{H_2} & \mathrm{CO} & \mathrm{O_2} & \mathrm{H_2O} & \mathrm{CO_2} \\ \mathrm{H} & 2 & 0 & 0 & 2 & 0 \\ \mathrm{C} & 0 & 1 & 0 & 0 & 1 \\ \mathrm{O} & 0 & 1 & 2 & 1 & 2 \end{array}; \qquad \rho = 3$$

$$\text{(d)}\quad \begin{array}{cccccccc} & \mathrm{CH_4} & \mathrm{H_2O} & \mathrm{CO} & \mathrm{CO_2} & \mathrm{H_2} & \mathrm{CH_3OH} & \mathrm{O_2} \\ \mathrm{H} & 4 & 2 & 0 & 0 & 2 & 4 & 0 \\ \mathrm{C} & 1 & 0 & 1 & 1 & 0 & 1 & 0 \\ \mathrm{O} & 0 & 1 & 1 & 2 & 0 & 1 & 2 \end{array}; \qquad \rho = 3$$

5. We employ the formula matrices obtained in problem 4. The substances in the formula matrices are numbered from the left to the right. To illustrate the method we reduce the reaction equations to zero but, of course, it is possible to rearrange them into their usual two-sided forms. Another reaction equations may also exist beyond the ones shown here. Let N and ρ be the number of the substances and the rank of the formula matrix, respectively. We apply the following procedure [25, 26]:

- determine $N - \rho$, the maximal number of the independent reactions;
- choose $N - \rho$ “free” unknowns whose values will be set arbitrarily;

- express the rest of the unknowns with the "free" ones and
- create $N-\rho$ linearly independent solutions by giving the value 1 to one of the free unknowns and 0 to the rest.

The detailed results are as follows:

(a) The equations for the conservations of the atomic species are:

$$\begin{aligned}\nu_4+2\nu_5+\nu_6&=0,\\ \nu_1+\nu_2&=0,\\ 2\nu_1+2\nu_3+2\nu_4+2\nu_5&=0,\\ 2\nu_2-2\nu_3-\nu_4+\nu_6&=0.\end{aligned}$$

The first set of reactions: we set the values of ν_2, ν_5 and ν_6; on the basis of the solutions

$$\begin{pmatrix}-1\\1\\1\\0\\0\\0\end{pmatrix},\quad \begin{pmatrix}0\\0\\1\\-2\\1\\0\end{pmatrix},\quad \begin{pmatrix}0\\0\\1\\-1\\0\\1\end{pmatrix},$$

we can write

$$\begin{aligned}-CaC_2O_4+Ca^{2+}+C_2O_4^{2-}&=0,\\ C_2O_4^{2-}-2HC_2O_4^{-}+H_2C_2O_4&=0,\\ C_2O_4^{2-}-HC_2O_4^{-}+H^{+}&=0.\end{aligned}$$

The second set of reactions: we set the values of ν_2, ν_4 and ν_6; on the basis of the solutions

$$\begin{pmatrix}-1\\1\\1\\0\\0\\0\end{pmatrix},\quad \frac{1}{2}\begin{pmatrix}0\\0\\-1\\2\\-1\\0\end{pmatrix},\quad \frac{1}{2}\begin{pmatrix}0\\0\\1\\0\\-1\\2\end{pmatrix},$$

omitting the factor 1/2, we find that

$$\begin{aligned}-CaC_2O_4+Ca^{2+}+C_2O_4^{2-}&=0,\\ -C_2O_4^{2-}+2HC_2O_4^{-}-H_2C_2O_4&=0,\\ C_2O_4^{2-}-H_2C_2O_4+2H^{+}&=0.\end{aligned}$$

(b) The equations for the conservations of the atomic species are

$$\begin{aligned} \nu_2 + 2\nu_3 + 3\nu_4 + \nu_5 + 2\nu_6 &= 0, \\ 3\nu_1 + 2\nu_2 + \nu_3 + \nu_5 &= 0, \\ 4\nu_1 + 4\nu_2 + 4\nu_3 + 4\nu_4 + \nu_5 + \nu_6 &= 0. \end{aligned}$$

The first set of reactions: we set the values of ν_1, ν_2 and ν_3; on the basis of the solutions

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \\ -3 \\ 3 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \\ 0 \\ -1 \\ -2 \\ 2 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 1 \\ -1 \\ -1 \\ 1 \end{pmatrix},$$

we can write

$$\begin{aligned} \mathrm{Na_3PO_4} - \mathrm{H_3PO_4} - 3\mathrm{NaOH} + 3\mathrm{H_2O} &= 0, \\ \mathrm{Na_2HPO_4} - \mathrm{H_3PO_4} - 2\mathrm{NaOH} + 2\mathrm{H_2O} &= 0, \\ \mathrm{NaH_2PO_4} - \mathrm{H_3PO_4} - \mathrm{NaOH} + \mathrm{H_2O} &= 0. \end{aligned}$$

The second set of reactions: we set the values of ν_1, ν_2 and ν_6; on the basis of the solutions

$$\begin{pmatrix} 1 \\ 0 \\ -3 \\ 2 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \\ -2 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 1 \\ -1 \\ -1 \\ 1 \end{pmatrix},$$

we can write

$$\begin{aligned} \mathrm{Na_3PO_4} - 3\mathrm{NaH_2PO_4} + 2\mathrm{H_3PO_4} &= 0, \\ \mathrm{Na_2HPO_4} - 2\mathrm{NaH_2PO_4} + \mathrm{H_3PO_4} &= 0, \\ \mathrm{NaH_2PO_4} - \mathrm{H_3PO_4} - \mathrm{NaOH} + \mathrm{H_2O} &= 0. \end{aligned}$$

(c) The equations for the conservations of the atomic species are

$$\begin{aligned} 2\nu_1 + 2\nu_4 &= 0, \\ \nu_2 + \nu_5 &= 0, \\ \nu_2 + 2\nu_3 + \nu_4 + 2\nu_5 &= 0. \end{aligned}$$

The first set of reactions: we set the values of ν_4 and ν_5; on the basis of the solutions

$$\frac{1}{2}\begin{pmatrix}-2\\0\\-1\\2\\0\end{pmatrix},\quad \frac{1}{2}\begin{pmatrix}0\\-2\\-1\\0\\2\end{pmatrix},$$

omitting the factor 1/2, we obtain

$$\begin{aligned}-2H_2 - O_2 + 2H_2O &= 0,\\ -2CO - O_2 + 2CO_2 &= 0.\end{aligned}$$

The second set of reactions: we set the values of ν_1 and ν_3; on the basis of the solutions

$$\begin{pmatrix}1\\-1\\0\\-1\\1\end{pmatrix},\quad \begin{pmatrix}0\\2\\1\\0\\-2\end{pmatrix},$$

we can write

$$\begin{aligned}H_2 - CO - H_2O + CO_2 &= 0,\\ 2CO + O_2 - 2CO_2 &= 0.\end{aligned}$$

(d) The equations for the conservations of the atomic species are

$$\begin{aligned}4\nu_1 + 2\nu_2 + 2\nu_5 + 4\nu_6 &= 0,\\ \nu_1 + \nu_3 + \nu_4 + \nu_6 &= 0,\\ \nu_2 + \nu_3 + 2\nu_4 + \nu_6 + 2\nu_7 &= 0.\end{aligned}$$

The first set of reactions: we set the values of ν_4, ν_5, ν_6 and ν_7; on the basis of the solutions

$$\frac{1}{3}\begin{pmatrix}1\\-2\\-4\\3\\0\\0\\0\end{pmatrix},\quad \frac{1}{3}\begin{pmatrix}-1\\-1\\1\\0\\3\\0\\0\end{pmatrix},\quad \frac{1}{3}\begin{pmatrix}-2\\-2\\-1\\0\\0\\3\\0\end{pmatrix},\quad \frac{1}{3}\begin{pmatrix}2\\-4\\-2\\0\\0\\0\\3\end{pmatrix},$$

omitting the factor $1/3$, we obtain

$$\begin{aligned}
CH_4 - 2H_2O - 4CO + 3CO_2 &= 0,\\
-CH_4 - H_2O + CO + 3H_2 &= 0,\\
-2CH_4 - 2H_2O - CO + 3CH_3OH &= 0,\\
2CH_4 - 4H_2O - 2CO + 3O_2 &= 0.
\end{aligned}$$

The second set of reactions: we set the values of ν_1, ν_2, ν_3 and ν_4; on the basis of the solutions

$$\frac{1}{2}\begin{pmatrix} 2\\0\\0\\0\\0\\-2\\1 \end{pmatrix}, \quad \frac{1}{2}\begin{pmatrix} 0\\2\\0\\0\\-2\\0\\-1 \end{pmatrix}, \quad \begin{pmatrix} 0\\0\\1\\0\\2\\-1\\0 \end{pmatrix}, \quad \frac{1}{2}\begin{pmatrix} 0\\0\\0\\2\\4\\-2\\-1 \end{pmatrix},$$

omitting the factor $1/2$, we find that

$$\begin{aligned}
2CH_4 - 2CH_3OH + O_2 &= 0,\\
2H_2O - 2H_2 - O_2 &= 0,\\
CO + 2H_2 - CH_3OH &= 0,\\
2CO_2 + 4H_2 - 2CH_3OH - O_2 &= 0.
\end{aligned}$$

For a “computerized” approach see [87].

6. The elimination of the substances $B_{i_1}, B_{i_2}, \ldots, B_{i_{R-1}}$ means that

$$\nu_{i_1} = \nu_{i_2} = \cdots = \nu_{i_{R-1}} = 0.$$

Using Eqn (1.19) this can be written as

$$\begin{aligned}
\nu_{i_1 1}c_1 + \nu_{i_1 2}c_2 + \cdots + \nu_{i_1 R}c_R &= 0\\
\nu_{i_2 1}c_1 + \nu_{i_2 2}c_2 + \cdots + \nu_{i_2 R}c_R &= 0\\
\vdots \quad &\vdots\\
\nu_{i_{R-1} 1}c_1 + \nu_{i_{R-1} 2}c_2 + \cdots + \nu_{i_{R-1} R}c_R &= 0.
\end{aligned} \tag{2.22}$$

We may assume – without loss of generality – that the first $R-1$ columns of the matrix of this system are linearly independent. Thus,

$$\begin{aligned}
\nu_{i_1 1}c_1 + \nu_{i_1 2}c_2 + \cdots + \nu_{i_1 R-1}c_{R-1} &= -\nu_{i_1 R}c_R \\
\nu_{i_2 1}c_1 + \nu_{i_2 2}c_2 + \cdots + \nu_{i_2 R-1}c_{R-1} &= -\nu_{i_2 R}c_R \\
\vdots \quad &\;\; \vdots \\
\nu_{i_{R-1} 1}c_1 + \nu_{i_{R-1} 2}c_2 + \cdots + \nu_{i_{R-1} R-1}c_{R-1} &= -\nu_{i_{R-1} R}c_R
\end{aligned} \tag{2.23}$$

and, from Cramer's rule,

$$c_j = \frac{D_j}{D}; \qquad j = 1, 2, \ldots, R-1,$$

where

$$D_j = \begin{vmatrix}
\nu_{i_1 1} & \nu_{i_1 2} & \cdots & \nu_{i_1 j-1} & -\nu_{i_1 R}c_R & \nu_{i_1 j+1} & \cdots & \nu_{i_1 R-1} \\
\nu_{i_2 1} & \nu_{i_2 2} & \cdots & \nu_{i_2 j-1} & -\nu_{i_2 R}c_R & \nu_{i_2 j+1} & \cdots & \nu_{i_2 R-1} \\
\vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\
\nu_{i_{R-1} 1} & \nu_{i_{R-1} 2} & \cdots & \nu_{i_{R-1} j-1} & -\nu_{i_{R-1} R}c_R & \nu_{i_{R-1} j+1} & \cdots & \nu_{i_{R-1} R-1}
\end{vmatrix}$$

and

$$D = \begin{vmatrix}
\nu_{i_1 1} & \nu_{i_1 2} & \cdots & \nu_{i_1 R-1} \\
\nu_{i_2 1} & \nu_{i_2 2} & \cdots & \nu_{i_2 R-1} \\
\vdots & \vdots & & \vdots \\
\nu_{i_{R-1} 1} & \nu_{i_{R-1} 2} & \cdots & \nu_{i_{R-1} R-1}
\end{vmatrix}.$$

By the application of some basic theorems on determinants $R-j-1$ swaps of columns lead to

$$D_j = (-1)^{R-j-1}(-c_R)d_j,$$

where

$$d_j = \begin{vmatrix}
\nu_{i_1 1} & \nu_{i_1 2} & \cdots & \nu_{i_1 j-1} & \nu_{i_1 j+1} & \cdots & \nu_{i_1 R} \\
\nu_{i_2 1} & \nu_{i_2 2} & \cdots & \nu_{i_2 j-1} & \nu_{i_2 j+1} & \cdots & \nu_{i_2 R} \\
\vdots & \vdots & & \vdots & \vdots & & \vdots \\
\nu_{i_{R-1} 1} & \nu_{i_{R-1} 2} & \cdots & \nu_{i_{R-1} j-1} & \nu_{i_{R-1} j+1} & \cdots & \nu_{i_{R-1} R}
\end{vmatrix}. \tag{2.24}$$

Notice that

$$(-1)^{R-j-1}(-c_R) = (-1)^{R+j}c_R.$$

On the basis of Eqn (1.19) the coefficients obtained by the elimination of the substances $B_{i_1}, B_{i_2}, \ldots, B_{i_{R-1}}$ can now be written as

$$\nu_i = \frac{c_R}{D}\sum_{j=1}^{R}(-1)^{R+j}\nu_{ij}d_j; \qquad i = 1,2,\ldots,N. \tag{2.25}$$

According to Eqn (2.24) the jth column of the $(R-1)\times(R-1)$ determinant d_j is absent. Thus, by expanding the determinant below with respect to its Rth row it is not difficult to see that

$$\nu_i = \frac{c_R}{D}\begin{vmatrix} \nu_{i_1 1} & \nu_{i_1 2} & \cdots & \nu_{i_1 R} \\ \nu_{i_2 1} & \nu_{i_2 2} & \cdots & \nu_{i_2 R} \\ \vdots & \vdots & & \vdots \\ \nu_{i_{R-1} 1} & \nu_{i_{R-1} 2} & \cdots & \nu_{i_{R-1} R} \\ \nu_{i1} & \nu_{i2} & \cdots & \nu_{iR} \end{vmatrix}; \qquad i = 1,2,\ldots,N.$$

7. (a) It is sufficient to find a matrix Q with which $\mathbf{QCQ}^{-1}$ will be a symmetric matrix. For $a \neq 0, b \neq 0$ and $c \neq 0$ let

$$\mathbf{Q} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}.$$

Thus,

$$\mathbf{Q}^{-1} = \begin{pmatrix} \frac{1}{a} & 0 & 0 \\ 0 & \frac{1}{b} & 0 \\ 0 & 0 & \frac{1}{c} \end{pmatrix},$$

since $\mathbf{QQ}^{-1} = \mathbf{Q}^{-1}\mathbf{Q} = \mathbf{I}$. To find appropriate values for a, b and c we utilize that

$$\mathbf{QCQ}^{-1} = \begin{pmatrix} -(k_1 + k_3') & \frac{ak_1'}{b} & \frac{ak_3}{c} \\ \frac{bk_1}{a} & -(k_1' + k_2) & \frac{bk_2'}{c} \\ \frac{ck_3'}{a} & \frac{ck_2}{b} & -(k_2' + k_3) \end{pmatrix}.$$

This matrix will be symmetrical if and only if

$$\begin{aligned} k_1\frac{b}{a} &= k_1'\frac{a}{b}, \\ k_2\frac{c}{b} &= k_2'\frac{b}{c}, \\ k_3\frac{a}{c} &= k_3'\frac{c}{a}, \end{aligned}$$

that is,

$$\frac{k_1}{k_1'} = \frac{a^2}{b^2}; \qquad \frac{k_2}{k_2'} = \frac{b^2}{c^2}; \qquad \frac{k_3}{k_3'} = \frac{c^2}{a^2}.$$

Because of Eqn (1.21) only two equations are independent from these three, and the system has infinitely many solutions. (When we multiply the three equations with each other it turns out that if Eqn (1.21) were not valid, the system of equations would be contradictory and this way of the symmetrization would not be possible.) For any positive solution (a, b, c) the symmetrized matrix will be

$$\mathbf{QCQ}^{-1} = \begin{pmatrix} -(k_1 + k_3') & \sqrt{k_1 k_1'} & \sqrt{k_3 k_3'} \\ \sqrt{k_1 k_1'} & -(k_1' + k_2) & \sqrt{k_2 k_2'} \\ \sqrt{k_3 k_3'} & \sqrt{k_2 k_2'} & -(k_2' + k_3) \end{pmatrix}.$$

Thus, we have proved that the eigenvalues of the matrix **C** are real.

(b) The eigenvalues can be determined from the characteristic equation

$$\begin{vmatrix} -(k_1 + k_3' + \lambda) & k_1' & k_3 \\ k_1 & -(k_1' + k_2 + \lambda) & k_2' \\ k_3' & k_2 & -(k_2' + k_3 + \lambda) \end{vmatrix} = 0,$$

whose expanded form is

$$\begin{aligned} &\lambda^3 + (k_1 + k_1' + k_2 + k_2' + k_3 + k_3')\lambda^2 + [k_1(k_2 + k_2' + k_3) \\ &+k_1'(k_2' + k_3 + k_3') + k_2(k_3 + k_3') + k_2'k_3']\lambda = 0. \end{aligned}$$

One of the roots of the characteristic equation is clearly $\lambda_1 = 0$, the other two roots can be computed from a quadratic equation. After the insertion of the numeric values this equation becomes treatably difficult and a straightforward calculation yields

$$\lambda_2 = (\sqrt{3} - 6)k_0 < 0; \qquad \lambda_3 = (-\sqrt{3} - 6)k_0 < 0.$$

It can be shown that if the principle of detailed balance holds, the eigenvalues of the kinetic matrix of any first-order reversible reaction system are non-positive real quantities, one of the latters is zero, and in the case of N substances the kinetic matrix has N linearly independent eigenvectors [88]. The time behaviour of the triangle reaction is discussed in [29].

8. Solving the characteristic equation

$$\begin{vmatrix} -(k_1+\lambda) & 0 & k_3 \\ k_1 & -(k_2+\lambda) & 0 \\ 0 & k_2 & -(k_3+\lambda) \end{vmatrix}$$

$$= -(k_1+\lambda)(k_2+\lambda)(k_3+\lambda) + k_1k_2k_3 = 0$$

we obtain the eigenvalues

$$\lambda_1 = 0,$$
$$\lambda_{2,3} = \frac{-(k_1+k_2+k_3) \pm \sqrt{D}}{2},$$

where

$$\begin{aligned} D &= (k_1+k_2+k_3)^2 - 4(k_1k_2 + k_1k_3 + k_2k_3) \\ &= (k_1+k_2-k_3)^2 - 4k_1k_2. \end{aligned}$$

It is easy to see that if the roots λ_2 and λ_3 are real then they are negative. If λ_2 and λ_3 are complex quantities then their real parts are negative. The roots λ_2 and λ_3 are complex if and only if the quantity D under the radical sign (the discriminant) is negative. A simple calculation shows that this occurs when, for example,

$$k_1 = 0.1k_0; \quad k_2 = 0.2k_0; \quad k_3 = 0.3k_0,$$

where $k_0 > 0$.

9. (a) The eigenvalues of the matrix **C** can be obtained from the equation

$$\begin{vmatrix} -k_1-\lambda & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 \\ k_1 & -k_2-\lambda & 0 & 0 & \dots & 0 & 0 & 0 & 0 \\ 0 & k_2 & -k_3-\lambda & 0 & \dots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & 0 & k_{N-2} & -k_{N-1}-\lambda & 0 \\ 0 & 0 & 0 & 0 & \dots & 0 & 0 & k_{N-1} & -\lambda \end{vmatrix} = 0.$$

The expansion of the determinant with respect to a row is easy since there are many zeros in the rows, and finally we have to take into account only the quantities in the main diagonal. The characteristic equation after expansion is

$$(-1)^N(k_1+\lambda)(k_2+\lambda)(k_3+\lambda)\cdots(k_{N-1}+\lambda)\lambda = 0,$$

from which the roots – the eigenvalues – can be read off simply:

$$\lambda_1 = -k_1; \quad \lambda_2 = -k_2; \ldots \lambda_{N-1} = -k_{N-1}; \quad \lambda_N = 0.$$

Thus, the eigenvalues are real non-positive quantities, and one of them is zero.

(b) From the characteristic equation

$$\begin{vmatrix} -\left(\sum_{i=1}^{N} k_i + \lambda\right) & 0 & 0 & 0 & \ldots & 0 & 0 \\ k_1 & -\lambda & 0 & 0 & \ldots & 0 & 0 \\ k_2 & 0 & -\lambda & 0 & \ldots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots \\ k_N & 0 & 0 & 0 & \ldots & 0 & -\lambda \end{vmatrix} = 0$$

we obtain

$$(-1)^{N+1}\left(\sum_{i=1}^{N} k_i + \lambda\right)\lambda^N = 0,$$

so the eigenvalues are

$$\lambda_1 = -\sum_{i=1}^{N} k_i; \quad \lambda_2 = \lambda_3 = \cdots = \lambda_{N+1} = 0.$$

Thus, the eigenvalues are non-positive real quantities, and N eigenvalues are equal to zero.

(c) Solving the characteristic equation

$$\begin{vmatrix} -(k_1+\lambda) & k_1' & 0 \\ k_1 & -(k_1'+k_2+\lambda) & 0 \\ 0 & k_2 & -\lambda \end{vmatrix}$$

$$= -\lambda^3 - (k_1+k_2+k_1')\lambda^2 - k_1k_2\lambda = 0,$$

we find the eigenvalues

$$\begin{aligned}\lambda_1 &= 0,\\ \lambda_{2,3} &= \frac{-(k_1+k_2+k_1') \pm \sqrt{(k_1+k_2+k_1')^2 - 4k_1k_2}}{2},\end{aligned} \tag{2.26}$$

According to Eqn (2.26) the $\lambda_{2,3}$ roots are negative if they are real. The transformation

$$\begin{aligned}D &= (k_1+k_2+k_1')^2 - 4k_1k_2\\ &= (k_1-k_2)^2 + k_1'^2 + 2k_1'(k_1+k_2) > 0\end{aligned}$$

of the expression under the radical sign (the discriminant) directly shows that $\lambda_{2,3}$ are real. Thus, the eigenvalues are non-positive, and one of them is zero.

10. (a) On the basis of Eqn (1.23) the system of equations for the stationary states of the intermediates is

$$\begin{pmatrix} 1 & -1 & 1 & -1\\ 0 & 1 & -1 & 0 \end{pmatrix}\begin{pmatrix} w_1\\ w_2\\ w_3\\ w_4 \end{pmatrix} = \begin{pmatrix} 0\\ 0 \end{pmatrix},$$

and its solution is

$$\begin{pmatrix} w_1\\ w_2\\ w_3\\ w_4 \end{pmatrix} = \begin{pmatrix} c_1\\ c_2\\ c_2\\ c_1 \end{pmatrix},$$

where c_1 and c_2 are arbitrary constants. Two linearly independent solutions – that is, “reaction routes” – are

$$\begin{pmatrix} 1\\ 0\\ 0\\ 1 \end{pmatrix}\begin{pmatrix} 0\\ 1\\ 1\\ 0 \end{pmatrix},$$

implying the reactions

$$\begin{aligned}\mathrm{A} &= \mathrm{E},\\ \mathrm{B} &= \mathrm{D},\end{aligned}$$

respectively.

(b) On the basis of Eqn (1.23) the system of equations for the stationary states of the intermediates is

$$\begin{pmatrix} 1 & -1 & -1 & 1 & -2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 & 1 & -1 & 0 & -1 & 0 & 0 & 0 \\ -1 & -1 & 0 & 0 & 0 & -1 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 2 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 1 & -2 \end{pmatrix} \begin{pmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ w_6 \\ w_7 \\ w_8 \\ w_9 \\ w_{10} \\ w_{11} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix},$$

from which

$$\begin{pmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ w_6 \\ w_7 \\ w_8 \\ w_9 \\ w_{10} \\ w_{11} \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ 2c_3 \\ \frac{1}{2}(c_1 - c_2 + c_3) \\ \frac{1}{2}(c_1 + c_2 + c_3) \\ \frac{1}{2}(c_1 + c_2 + c_3) \\ c_1 + c_2 \\ c_1 + c_2 \\ 2c_3 \\ c_3 \end{pmatrix}, \qquad (2.27)$$

where c_1, c_2 and c_3 are arbitrarily chosen quantities. With the choices (2 0 0), (0 2 0) and (0 0 2) for $(c_1\ c_2\ c_3)$ we obtain three linearly independent solutions – that is, three "reaction routes" –, which can be easily determined by the aid of Eqn (2.27). It is interesting that all the three routes have the same reaction equation,

$$\mathrm{BrO_3^-} + 3\mathrm{RH} + \mathrm{H^+} = 2\mathrm{ROH} + \mathrm{RBr} + \mathrm{H_2O}.$$

11. (a) Let the coordinates of an arbitrary vector and its image be (x, y, z) and (x', y', z'), respectively. Because of the special position of the reflecting

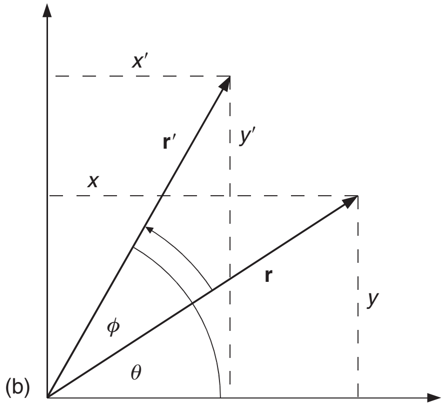


Figure 2.6 A rotation by the angle ϕ around the axis z

plane it is obvious that $x' = x$, $y' = -y$ and $z' = z$, so

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

The 3 × 3 matrix on the right-hand side is the matrix of the transformation. On the basis of Fig. 2.6 $z' = z$ moreover

$$x' = r\cos(\theta + \phi) = r(\cos\theta\cos\phi - \sin\theta\sin\phi)$$

and

$$y' = r\sin(\theta + \phi) = r(\sin\theta\cos\phi + \cos\theta\sin\phi).$$

Since

$$x = r\cos\theta$$

and

$$y = r\sin\theta,$$

it follows that

$$x' = x\cos\phi - y\sin\phi$$

and

$$y' = x\sin\phi + y\cos\phi.$$

This implies

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix},$$

and the 3×3 matrix on the right-hand side is the matrix of the transformation.

Simple matrix multiplications (and in the second case $\sin^2\phi + \cos^2\phi = 1$) yield

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and

$$\begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Thus, these matrices are orthogonal.

12. We investigate homogeneous linear systems of equations. Such a system has a non-trivial solution, that is, a solution that differs from zero if and only if its determinant is zero. In the following we present the solutions of the given systems of equations as column matrices. In the latters $a, a_1, a_2, \ldots,$ etc. denote arbitrary constants.

(a) $\begin{vmatrix} m & 1 \\ 1 & m \end{vmatrix} = m^2 - 1 = 0$

$$m = 1 : \begin{pmatrix} a \\ -a \end{pmatrix}; \quad m = -1 : \begin{pmatrix} a \\ a \end{pmatrix}.$$

Energies: $\alpha + \beta < \alpha - \beta$.

(b) $$\begin{vmatrix} m & 1 & 1 \\ 1 & m & 1 \\ 1 & 1 & m \end{vmatrix} = (m+2)(m-1)^2 = 0$$

$$m_1 = -2 : \begin{pmatrix} a \\ a \\ a \end{pmatrix}; \quad m_{2,3} = 1 : \begin{pmatrix} a_1 \\ a_2 \\ -(a_1 + a_2) \end{pmatrix}$$

Energies: $\alpha + 2\beta < \alpha - \beta$.

(c) $$\begin{vmatrix} m & 1 & 0 \\ 1 & m & 1 \\ 0 & 1 & m \end{vmatrix} = m(m^2 - 2) = 0$$

$$m_1 = 0 : \begin{pmatrix} a \\ 0 \\ -a \end{pmatrix}; \quad m_2 = \sqrt{2} : \begin{pmatrix} a \\ -\sqrt{2}a \\ a \end{pmatrix}; \quad m_3 = -\sqrt{2} : \begin{pmatrix} a \\ \sqrt{2}a \\ a \end{pmatrix}$$

Energies: $\alpha + \sqrt{2}\beta < \alpha < \alpha - \sqrt{2}\beta$.

(d) $$\begin{vmatrix} m & 1 & 0 & 1 \\ 1 & m & 1 & 0 \\ 0 & 1 & m & 1 \\ 1 & 0 & 1 & m \end{vmatrix} = m^2(m^2 - 4) = 0$$

$$m_{1,2} = 0 : \begin{pmatrix} a_1 \\ a_2 \\ -a_1 \\ -a_2 \end{pmatrix}; \qquad m_3 = 2 : \begin{pmatrix} a \\ -a \\ a \\ -a \end{pmatrix};$$

$$m_4 = -2 : \begin{pmatrix} a \\ a \\ a \\ a \end{pmatrix}.$$

Energies: $\alpha + 2\beta < \alpha < \alpha - 2\beta$.

(e) $$\begin{vmatrix} m & 1 & 0 & 0 \\ 1 & m & 1 & 0 \\ 0 & 1 & m & 1 \\ 0 & 0 & 1 & m \end{vmatrix} = (m^2 + m - 1)(m^2 - m - 1) = 0$$

$$m_1 = \frac{\sqrt{5}+1}{2} : \begin{pmatrix} a \\ -\frac{\sqrt{5}+1}{2}a \\ \frac{\sqrt{5}+1}{2}a \\ -a \end{pmatrix}; \qquad m_2 = \frac{\sqrt{5}-1}{2} : \begin{pmatrix} a \\ \frac{1-\sqrt{5}}{2}a \\ \frac{1-\sqrt{5}}{2}a \\ a \end{pmatrix};$$

$$m_3 = \frac{1-\sqrt{5}}{2} : \begin{pmatrix} a \\ -\frac{1-\sqrt{5}}{2}a \\ \frac{1-\sqrt{5}}{2}a \\ -a \end{pmatrix}; \qquad m_4 = -\frac{1+\sqrt{5}}{2} : \begin{pmatrix} a \\ \frac{\sqrt{5}+1}{2}a \\ \frac{\sqrt{5}+1}{2}a \\ a \end{pmatrix}.$$

Energies:

$$\alpha + \frac{\sqrt{5}+1}{2}\beta < \alpha + \frac{\sqrt{5}-1}{2}\beta < \alpha - \frac{\sqrt{5}-1}{2}\beta$$
$$< \alpha - \frac{\sqrt{5}+1}{2}\beta.$$

(f) $$\begin{vmatrix} m & 1 & 0 & 0 & 0 & 1 \\ 1 & m & 1 & 0 & 0 & 0 \\ 0 & 1 & m & 1 & 0 & 0 \\ 0 & 0 & 1 & m & 1 & 0 \\ 0 & 0 & 0 & 1 & m & 1 \\ 1 & 0 & 0 & 0 & 1 & m \end{vmatrix} = (m+2)(m-2)(m+1)^2(m-1)^2 = 0$$

$$m_1 = -2 : \begin{pmatrix} a \\ a \\ a \\ a \\ a \\ a \end{pmatrix}; \qquad m_2 = 2 : \begin{pmatrix} a \\ -a \\ a \\ -a \\ a \\ -a \end{pmatrix};$$

$$m_{3,4} = -1 : \begin{pmatrix} a_1 \\ a_2 \\ -a_1 + a_2 \\ -a_1 \\ -a_2 \\ a_1 - a_2 \end{pmatrix}; \qquad m_{5,6} = 1 : \begin{pmatrix} a_1 \\ a_2 \\ -a_1 - a_2 \\ a_1 \\ a_2 \\ -a_1 - a_2 \end{pmatrix}.$$

Energies:

$$\alpha + 2\beta < \alpha + \beta < \alpha - \beta < \alpha - 2\beta.$$

2.3 DERIVATIVE AND INTEGRAL

1. (a) On the basis of Eqn (1.24)

$$H_0(x) = (-1)^0 e^{x^2} e^{-x^2} = 1,$$

$$H_1(x) = (-1)^1 e^{x^2} \frac{\mathrm{d}}{\mathrm{d}x} e^{-x^2} = -e^{x^2}\left(-2xe^{-x^2}\right) = 2x,$$

$$\begin{aligned} H_2(x) &= (-1)^2 e^{x^2} \frac{\mathrm{d}^2}{\mathrm{d}x^2} e^{-x^2} \\ &= (-1)^2 e^{x^2} \frac{\mathrm{d}}{\mathrm{d}x}\left(-2xe^{-x^2}\right) \\ &= 4x^2 - 2, \end{aligned}$$

$$\begin{aligned} H_3(x) &= (-1)^3 e^{x^2} \frac{\mathrm{d}^3}{\mathrm{d}x^3}\left(e^{-x^2}\right) \\ &= (-1)^3 e^{x^2} \frac{\mathrm{d}}{\mathrm{d}x}\left[(4x^2 - 2)e^{-x^2}\right] \\ &= 8x^3 - 12x, \end{aligned}$$

$$\begin{aligned} H_4(x) &= (-1)^4 e^{x^2} \frac{\mathrm{d}^4}{\mathrm{d}x^4}\left(e^{-x^2}\right) \\ &= (-1)^4 e^{x^2} \frac{\mathrm{d}}{\mathrm{d}x}\left[(-8x^3 + 12x)e^{-x^2}\right] \\ &= 16x^4 - 48x^2 + 12, \end{aligned}$$

$$\begin{aligned}H_5(x) &= (-1)^5 e^{x^2}\frac{\mathrm{d}^5}{\mathrm{d}x^5}\left(e^{-x^2}\right)\\ &= (-1)^5 e^{x^2}\frac{\mathrm{d}}{\mathrm{d}x}\left[(16x^4-48x^2+12)e^{-x^2}\right]\\ &= 32x^5-160x^3+120x.\end{aligned}$$

Notice that

$$H_{n+1}(x) = -e^{x^2}\frac{\mathrm{d}}{\mathrm{d}x}\left[H_n(x)e^{-x^2}\right], \tag{2.28}$$

where $n = 0, 1, 2 \ldots$.

(b) i. Since $(-x)^n = (-1)^n x^n$, we can write that

$$\begin{aligned}H_n(-x) &= (-1)^n e^{(-x)^2}\frac{\mathrm{d}^n}{\mathrm{d}(-x)^n}e^{-(-x)^2}\\ &= \frac{(-1)^n}{(-1)^n}e^{(-x)^2}\frac{\mathrm{d}^n}{\mathrm{d}x^n}e^{-(-x)^2}\\ &= (-1)^n(-1)^n e^{x^2}\frac{\mathrm{d}^n}{\mathrm{d}x^n}e^{-x^2}\\ &= (-1)^n H_n(x).\end{aligned}$$

ii. the first derivative of H_n is

$$\begin{aligned}\frac{\mathrm{d}H_n}{\mathrm{d}x}(x) &= (-1)^n\frac{\mathrm{d}}{\mathrm{d}x}\left(e^{x^2}\frac{\mathrm{d}^n}{\mathrm{d}x^n}e^{-x^2}\right)\\ &= (-1)^n\left[2xe^{x^2}\frac{\mathrm{d}^n}{\mathrm{d}x^n}e^{-x^2}+e^{x^2}\frac{\mathrm{d}^{n+1}}{\mathrm{d}x^{n+1}}e^{-x^2}\right] \qquad (2.29)\\ &= 2xH_n(x)-H_{n+1}(x),\end{aligned}$$

from which

$$H_{n+1}(x) = 2xH_n(x) - \frac{\mathrm{d}H_n}{\mathrm{d}x}(x). \tag{2.30}$$

For a proof involving a mathematical induction we verify the statement for the first few values of n by the aid of paragraph 1a and then assume that

$$\frac{\mathrm{d}H_n}{\mathrm{d}x}(x) = 2nH_{n-1}(x). \tag{2.31}$$

From Eqn (2.30)

$$\frac{\mathrm{d}H_{n+1}}{\mathrm{d}x}(x) = 2H_n(x) + 2x\frac{\mathrm{d}H_n}{\mathrm{d}x}(x) - \frac{\mathrm{d}^2H_n}{\mathrm{d}x^2}(x),$$

which, utilizing Eqn (2.31), leads to

$$\begin{aligned}\frac{\mathrm{d}H_{n+1}}{\mathrm{d}x}(x) &= 2H_n(x) + 4nxH_{n-1}(x) - \frac{\mathrm{d}^2H_n}{\mathrm{d}x^2}(x)\\ &= 2H_n(x) + 4nxH_{n-1}(x) - 2n\frac{\mathrm{d}H_{n-1}}{\mathrm{d}x}(x).\end{aligned}$$

It follows from Eqn (2.29) that

$$\frac{\mathrm{d}H_{n-1}}{\mathrm{d}x}(x) = 2xH_{n-1}(x) - H_n(x),$$

and using this

$$\begin{aligned}\frac{\mathrm{d}H_{n+1}}{\mathrm{d}x}(x) &= 2H_n(x) + 4nxH_{n-1}(x)\\ &\quad -2n\left[2xH_{n-1}(x) - H_n(x)\right]\\ &= 2(n+1)H_n(x),\end{aligned}$$

which completes the proof.

iii. This follows very simply from Eqn (2.30) and the already proved Eqn (2.31).

iv. For $n = 0$ the statement is not valid. In the case of $n > 0$ the integration can be accomplished in the following way:

$$\begin{aligned}\int_{-\infty}^{\infty} H_n(x)e^{-x^2}\mathrm{d}x &= \int_{-\infty}^{\infty} (-1)^n\frac{\mathrm{d}^n}{\mathrm{d}x^n}e^{-x^2}\mathrm{d}x\\ &= (-1)^n\left[\frac{\mathrm{d}^{n-1}}{\mathrm{d}x^{n-1}}e^{-x^2}\right]_{-\infty}^{\infty}\\ &= -\left[H_{n-1}(x)e^{-x^2}\right]_{-\infty}^{\infty}.\end{aligned}$$

The square bracket in the last line is evidently zero since the limits of the expression at infinity are determined by the exponential function.

v. Let $m = n$. Using Eqn (2.28) we obtain

$$\int_{-\infty}^{\infty} H_n^2(x)e^{-x^2}\mathrm{d}x = -\int_{-\infty}^{\infty} H_n(x)\frac{\mathrm{d}}{\mathrm{d}x}\left[H_{n-1}(x)e^{-x^2}\right]\mathrm{d}x,$$

which, applying integration by parts and Eqn (2.31), leads to

$$\begin{aligned}\int_{-\infty}^{\infty} H_n^2(x)e^{-x^2}\mathrm{d}x &= -\left[H_n(x)H_{n-1}(x)e^{-x^2}\right]_{-\infty}^{\infty} \\ &\quad +\int_{-\infty}^{\infty} \frac{\mathrm{d}H_n}{\mathrm{d}x}(x)H_{n-1}(x)e^{-x^2}\mathrm{d}x \\ &= 2n\int_{-\infty}^{\infty} H_{n-1}^2(x)e^{-x^2}\mathrm{d}x.\end{aligned}$$

Recursive applications of the formula obtained give

$$\int_{-\infty}^{\infty} H_n^2(x)e^{-x^2}\mathrm{d}x = 2^n n!\int_{-\infty}^{\infty} H_0^2(x)e^{-x^2}\mathrm{d}x = 2^n n!\sqrt{\pi}.$$

Now let $m \neq n$. If m is odd and n is even or conversely then, because of paragraph 1b, the integrand of the integral investigated is an odd function. So we know without any additional consideration that the integral is zero provided it exists. For an accurate proof we use similar considerations as above:

$$\begin{aligned}\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2}\mathrm{d}x &= \int_{-\infty}^{\infty} \frac{\mathrm{d}H_m}{\mathrm{d}x}(x)H_{n-1}(x)e^{-x^2}\mathrm{d}x \\ &= 2m\int_{-\infty}^{\infty} H_{m-1}(x)H_{n-1}(x)e^{-x^2}\mathrm{d}x.\end{aligned}$$

If $m > n$, recursive applications of the formula obtained yield

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2}\mathrm{d}x = 2^n\frac{m!}{(m-n)!}\int_{-\infty}^{\infty} H_{m-n}(x)e^{-x^2}\mathrm{d}x.$$

By virtue of paragraph 1(b) iv, however, the last integral is zero.

2. (a) On the basis of Eqn (1.25)

$$P_0^0(x) = 1; \qquad P_1^0(x) = x,$$

$$P_1^1(x) = (1-x^2)^{1/2}; \qquad P_2^0(x) = \frac{1}{2}(3x^2-1),$$

$$P_2^1(x) = 3x(1-x^2)^{1/2}; \qquad P_2^2(x) = 3(1-x^2),$$

$$P_3^0(x) = \frac{1}{2}x(5x^2-3); \qquad P_3^1(x) = \frac{3}{2}(1-x^2)^{1/2}(5x^2-1),$$

$$P_3^2(x) = 15x(1-x^2); \qquad P_3^3(x) = 15(1-x^2)^{3/2},$$

$$P_4^0(x) = \frac{1}{8}(35x^4-30x^2+3),$$

$$P_4^1(x) = \frac{5}{2}x(1-x^2)^{1/2}(7x^2-3),$$

$$P_4^2(x) = \frac{15}{2}(1-x^2)(7x^2-1),$$

$$P_4^3(x) = 105x(1-x^2)^{3/2}; \qquad P_4^4(x) = 105(x^2-1)^2,$$

$$P_5^0(x) = \frac{1}{8}x(63x^4-70x^2+15),$$

$$P_5^1(x) = \frac{15}{8}(1-x^2)^{1/2}(21x^4-14x^2+1),$$

$$P_5^2(x) = \frac{105}{2}x(1-x^2)(3x^2-1),$$

$$P_5^3(x) = \frac{105}{2}(1-x^2)^{3/2}(9x^2-1),$$

$$P_5^4(x) = 945x(x^2-1)^2; \qquad P_5^5(x) = 945(1-x^2)^{5/2}.$$

(b) In the polynomial $x(x^2-1)^l$ the powers x^{2l+1}, x^{2l-1}, $x^{2l-3}, \ldots$ occur. The only term that contributes to the $2l$th derivative of the polynomial is that of the highest degree, the other terms cease during the subsequent differentiations. Taking into account the derivatives of the term of the highest degree we can write that

$$\frac{\mathrm{d}^{2l}}{\mathrm{d}x^{2l}}x(x^2-1)^l = (2l+1)2l(2l-1)\cdot \cdots \cdot 2\cdot x = (2l+1)!x.$$

By similar considerations

$$\frac{d^{2l}}{dx^{2l}}(x^2-1)^l = 2l(2l-1)\cdot\cdots\cdot 2\cdot 1 = (2l)!.$$

We reformulate $P_{l+1}^l(x)$ in this way:

$$P_{l+1}^l(x) = \left[2^{l+1}(l+1)!\right]^{-1}(1-x^2)^{l/2}\frac{d^{2l+1}}{dx^{2l+1}}(x^2-1)^{l+1},$$
$$P_{l+1}^l(x) = \left[2^{l+1}(l+1)!\right]^{-1}(1-x^2)^{l/2}\frac{d^{2l}}{dx^{2l}}\frac{d}{dx}(x^2-1)^{l+1},$$
$$P_{l+1}^l(x) = \left[2^l l!\right]^{-1}(1-x^2)^{l/2}\frac{d^{2l}}{dx^{2l}}x(x^2-1)^l,$$
$$P_{l+1}^l(x) = \left[2^l l!\right]^{-1}(1-x^2)^{l/2}(2l+1)!x.$$

If we compare the last equation with the second equation of the transformation

$$P_l^l(x) = \left[2^l l!\right]^{-1}(1-x^2)^{l/2}\frac{d^{2l}}{dx^{2l}}(x^2-1)^l,$$
$$P_l^l(x) = \left[2^l l!\right]^{-1}(1-x^2)^{l/2}(2l)!,$$

the statement becomes evident.

(c) In the case of $m > l$ we also have $l+m > 2l$. Since $(x^2-1)^l$ is a polynomial of degree $2l$, it follows that

$$\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l = 0.$$

From this $P_l^m(x) = 0$ would follow for any x.

(d) First we investigate the case when the values of l are different:

$$\begin{aligned}\int_{-1}^{1} P_2^1(x)P_4^1(x)\,dx &= \int_{-1}^{1} 3x(1-x^2)^{1/2}\frac{5}{2}x(1-x^2)^{1/2}(7x^2-3)\,dx\\ &= \frac{15}{2}\int_{-1}^{1}(-7x^6+10x^4-3x^2)\,dx\\ &= \frac{15}{2}\left[-x^7+2x^5-x^3\right]_{-1}^{1} = 0.\end{aligned}$$

In the case of $l = k = 2$

$$\begin{aligned}\int_{-1}^{1} P_2^1(x) P_2^1(x) &= \int_{-1}^{1} 9x^2(1-x^2)\,\mathrm{d}x \\ &= \left[\frac{x^3}{3} - \frac{x^5}{5}\right]_{-1}^{1} = \frac{12}{5} = \frac{2}{2\cdot 2+1}\frac{(2+1)!}{(2-1)!}1,\end{aligned}$$

while in the case of $l = k = 4$

$$\begin{aligned}\int_{-1}^{1} P_4^1(x) P_4^1(x) &= \frac{25}{4}\left[-\frac{49x^9}{9} + \frac{91x^7}{7} - \frac{51x^5}{5} + \frac{9x^3}{3}\right]_{-1}^{1} \\ &= \frac{40}{9} = \frac{2}{2\cdot 4+1}\frac{(4+1)!}{(4-1)!}1.\end{aligned}$$

3. (a) $L_1^k(x) = -x + k + 1,$

$$\begin{aligned}L_2^k(x) &= \tfrac{1}{2}\left[x^2 - 2(k+2)x + (k+1)(k+2)\right], \\ L_3^k(x) &= -\tfrac{1}{6}\left[x^3 - 3(k+3)x^2 + 3(k+2)(k+3)x\right. \\ &\qquad \left. - (k+1)(k+2)(k+3)\right], \\ L_4^k(x) &= \tfrac{1}{24}\left[x^4 - 4(k+4)x^3 + 6(k+3)(k+4)x^2\right. \\ &\qquad \left. - 4(k+2)(k+3)(k+4)x + (k+1)(k+2)(k+3)(k+4)\right], \\ L_5^k(x) &= -\tfrac{1}{120}\left[x^5 - 5(k+5)x^4 + 10(k+4)(k+5)x^3\right. \\ &\qquad -10(k+3)(k+4)(k+5)x^2 \\ &\qquad +5(k+2)(k+3)(k+4)(k+5)x \\ &\qquad \left. - (k+1)(k+2)(k+3)(k+4)(k+5)\right].\end{aligned}$$

(b) First we derive the formula to be used later. For $a > 0$ we have

$$\int_0^\infty e^{-ax} = \frac{1}{a}. \tag{2.32}$$

If $a > 0$ and $b = 1, 2, 3, \ldots$, integration by parts yields

$$\begin{aligned}\int_0^\infty e^{-ax} x^b\,\mathrm{d}x &= -\left[\frac{e^{-ax}x^b}{a}\right]_0^\infty + \frac{b}{a}\int_0^\infty e^{-ax}x^{b-1}\,\mathrm{d}x \\ &= \frac{b}{a}\int_0^\infty e^{-ax}x^{b-1}\,\mathrm{d}x.\end{aligned}$$

For the integral containing x^{b-1} we can apply again the formula just obtained, and the recursive procedure can be repeated until x^0 occurs in the integral on the right-hand side:

$$\int_0^\infty e^{-ax}x^b \,\mathrm{d}x = \frac{b(b-1)\cdot \cdots \cdot 1}{a^b}\int_0^\infty e^{-ax}\,\mathrm{d}x.$$

Using now Eqn (2.32) we find that

$$\int_0^\infty e^{-ax}x^b \,\mathrm{d}x = \frac{b!}{a^{b+1}} \tag{2.33}$$

for $a > 0$ and $b = 0, 1, 2, \ldots$. Applying this formula

$$\int_0^\infty e^{-x}x^{n+k} \,\mathrm{d}x = (n+k)! \tag{2.34}$$

for $n, k = 0, 1, 2, \ldots$. Determining the product $L_2^k(x)L_3^k(x)$ on the basis of paragraph 3a, and applying Eqn (2.34) we obtain

$$\begin{aligned}\int_0^\infty e^{-x}x^k L_2^k(x)L_3^k(x)\,\mathrm{d}x = &-\frac{(k+3)!}{12}\\ &\times [(k+5)(k+4) - (5k+13)(k+4)\\ &\quad + (k+2)(10k+28) - (k+2)(10k+16)\\ &\quad + 4(k+1)(k+2)]\\ = &-\frac{(k+3)!}{12}0 = 0.\end{aligned}$$

By a similar method

$$\begin{aligned}\int_0^\infty e^{-x}x^k [L_2^k(x)]^2\,\mathrm{d}x = &\frac{(k+2)!}{2\cdot 2!}[(k+4)(k+3) - 4(k+2)(k+3)\\ &+ 2(k+2)(3k+5) - 3(k+1)(k+2)]\\ = &\frac{(k+2)!}{2!}\end{aligned}$$

and, omitting the detailed calculations,

$$\int_0^\infty e^{-x}x^k [L_3^k(x)]^2\,\mathrm{d}x = \frac{(k+3)!}{3!}.$$

4. In the following we neglect the root $r_\mathrm{m} = 0$ whenever it occurs because this is not an inner point of the domain of definition.

   The first derivative of the function,

$$\frac{\mathrm{d}P_{10}}{\mathrm{d}r}(r) = 8\left(\frac{Z}{a_0}\right)^3 e^{-(2Zr/a_0)}\left(r - \frac{Zr^2}{a_0}\right),$$

vanishes at the inner point

$$r_\mathrm{m} = \frac{a_0}{Z}. \tag{2.35}$$

For the second derivative,

$$\frac{\mathrm{d}^2P_{10}}{\mathrm{d}r^2}(r) = 8\left(\frac{Z}{a_0}\right)^3 e^{-(2Zr/a_0)}\left(1 - \frac{4Zr}{a_0} + \frac{2Z^2r^2}{a_0^2}\right),$$

we may write at $r = r_\mathrm{m}$ that

$$\frac{\mathrm{d}^2P_{10}}{\mathrm{d}r^2}(r_\mathrm{m}) = -8\left(\frac{Z}{a_0}\right)^3 e^{-2} < 0.$$

Thus, P_{10} has a local maximum at the value given by Eqn (2.35).

5. Let

$$\phi_1(r) = \phi(\hat{\rho}(r)) = \phi\left(\frac{Zr}{a_0}\right),$$

where ϕ is any function in the problem. According to the chain rule of differentiation

$$\phi_1'(r) = \phi'(\hat{\rho}(r))\hat{\rho}'(r) = \phi'(\hat{\rho}(r))\frac{Z}{a_0}$$

and

$$\phi_1''(r) = \phi''(\hat{\rho}(r))[\hat{\rho}'(r)]^2 = \phi''(\hat{\rho}(r))\frac{Z^2}{a_0^2},$$

from which it follows that there exists an one-to-one connection between the local extrema of ϕ_1 and ϕ and it is sufficient to investigate the extrema of ϕ as a function of $\rho = \hat{\rho}(r)$. In the following we neglect the root $r_\mathrm{m} = 0$ whenever it occurs because this is not an inner point of the domain of definition.

(a)

$$\phi(\rho) = (2-\rho)e^{-(1/2)\rho},$$
$$\frac{\mathrm{d}\phi}{\mathrm{d}\rho}(\rho_\mathrm{m}) = e^{-(1/2)\rho_\mathrm{m}}\left(\frac{1}{2}\rho_\mathrm{m} - 2\right) = 0,$$

from which

$$\rho_\mathrm{m} = 4, \quad r_\mathrm{m} = a_0\rho_\mathrm{m} = 212\,\mathrm{pm}.$$

On the basis of the formula

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}\rho^2}(\rho_\mathrm{m}) = \frac{1}{2}e^{-2} > 0$$

a local minimum occurs at ρ_m.

(b)

$$\phi(\rho) = \rho e^{-(1/2)\rho},$$
$$\phi'(\rho_\mathrm{m}) = e^{-(1/2)\rho_\mathrm{m}}\left(1 - \frac{1}{2}\rho_\mathrm{m}\right) = 0,$$

so a local extremum can only occur at

$$\rho_\mathrm{m} = 2, \quad r_\mathrm{m} = a_0\rho_\mathrm{m} = 106\,\mathrm{pm}.$$

Since

$$\phi''(\rho_\mathrm{m}) = -\frac{1}{2}e^{-1} < 0,$$

a local maximum is attained at ρ_m. We remark that the existence of a local maximum can already be inferred from $\phi(\rho) > 0$ and

$$\lim_{\rho\to 0}\phi(\rho) = \lim_{\rho\to\infty}\phi(\rho) = 0.$$

(c)

$$\phi(\rho) = (27 - 18\rho + 2\rho^2)e^{-(1/3)\rho},$$
$$\phi'(\rho_\mathrm{m}) = -\frac{1}{3}e^{-(1/3)\rho_\mathrm{m}}(2\rho_\mathrm{m}^2 - 30\rho_\mathrm{m} + 81) = 0,$$
$$\rho_{\mathrm{m}1,2} = \frac{30 \pm 6\sqrt{7}}{4}; \quad r_{\mathrm{m}1} = 607\,\mathrm{pm}; \quad r_{\mathrm{m}2} = 187\,\mathrm{pm},$$
$$\phi''(\rho_{\mathrm{m}1,2}) = \mp 2\sqrt{7}e^{\frac{\mp\sqrt{7}-5}{2}}.$$

Thus, at $\rho_{\mathrm{m}1}$ a local maximum while at $\rho_{\mathrm{m}2}$ a local minimum occurs.

(d)

$$\begin{aligned}
\phi(\rho) &= (6\rho - \rho^2)e^{-(1/3)\rho}, \\
\phi'(\rho_{\mathrm{m}}) &= \frac{1}{3}e^{-(1/3)\rho_{\mathrm{m}}}(\rho_{\mathrm{m}}^2 - 12\rho_{\mathrm{m}} + 18) = 0, \\
\rho_{\mathrm{m}1,2} &= 6 \pm 3\sqrt{2}; \quad r_{\mathrm{m}1} = 542\,\mathrm{pm}; \quad r_{\mathrm{m}2} = 93\,\mathrm{pm}, \\
\phi''(\rho_{\mathrm{m}1,2}) &= \pm 2\sqrt{2}e^{\mp\sqrt{2}-2}.
\end{aligned}$$

According to this calculation the function exhibits a local minimum at $\rho_{\mathrm{m}1}$ and a local maximum at $\rho_{\mathrm{m}2}$.

(e)

$$\begin{aligned}
\phi(\rho) &= \rho^2 e^{-(1/3)\rho}, \\
\phi'(\rho_{\mathrm{m}}) &= \frac{1}{3}e^{-(1/3)\rho_{\mathrm{m}}}\rho_{\mathrm{m}}(6 - \rho_{\mathrm{m}}) = 0, \\
\rho_{\mathrm{m}} &= 6; \quad r_{\mathrm{m}} = 318\,\mathrm{pm}, \\
\phi''(\rho_{\mathrm{m}}) &= -2e^{-2} < 0.
\end{aligned}$$

This means a local maximum at ρ_{m}, and this is the only local extremum.

6. Utilizing the formula $\rho = \hat{\rho}(r)$ we transform the integral:

$$\langle r \rangle = \left(\frac{a_0}{Z}\right)^4 \int_0^\infty \left|R_{nl}\left(\frac{a_0\rho}{Z}\right)\right|^2 \rho^3 \,\mathrm{d}\rho.$$

The formula necessary to the calculation has been derived in the solution of problem 3b:

$$\int_0^\infty x^b e^{-ax}\,\mathrm{d}x = \frac{b!}{a^{b+1}} \qquad (a > 0;\ b = 0, 1, 2, \ldots).$$

(a)

$$\langle r \rangle = 4\frac{a_0}{Z}\int_0^\infty \rho^3 e^{-2\rho}\,\mathrm{d}\rho = \frac{3}{2}\frac{a_0}{Z}$$

(b)

$$\langle r \rangle = \frac{1}{24}\frac{a_0}{Z}\int_0^\infty \rho^5 e^{-\rho}\,\mathrm{d}\rho = 5\frac{a_0}{Z}$$

(c)

$$\langle r\rangle = \frac{4}{3\cdot 81^2}\frac{a_0}{Z}\int_0^\infty (27-18\rho+2\rho^2)^2\rho^3 e^{-(2/3)\rho}\,\mathrm{d}\rho = \frac{27}{2}\frac{a_0}{Z}.$$

7. (a) First we calculate the integrals to be applied. Let α be a non-zero constant. Employing integration by parts and the formula $\sin^2\alpha x + \cos^2\alpha x = 1$ we obtain

$$\begin{aligned}\int \sin^2\alpha x\,\mathrm{d}x &= \int (\sin\alpha x)(\sin\alpha x)\,\mathrm{d}x\\ &= -\frac{\sin\alpha x\cos\alpha x}{\alpha} + \int (1-\sin^2\alpha x)\,\mathrm{d}x,\end{aligned}$$

and the decomposition of the integral on the right-hand side followed by a rearrangement and the application of

$$\sin 2\alpha x = 2\sin\alpha x\cos\alpha x$$

leads to the formula

$$\int \sin^2\alpha x\,\mathrm{d}x = -\frac{\sin 2\alpha x}{4\alpha} + \frac{1}{2}\int 1\,\mathrm{d}x = -\frac{\sin 2\alpha x}{4\alpha} + \frac{1}{2}x + C. \quad (2.36)$$

The following integral is also determined with the help of integration by parts and Eqn (2.36):

$$\int x\sin^2\alpha x\,\mathrm{d}x = x\left(-\frac{\sin 2\alpha x}{4\alpha} + \frac{1}{2}x\right) - \int\left(-\frac{\sin 2\alpha x}{4\alpha} + \frac{1}{2}x\right)\mathrm{d}x$$

so

$$\int x\sin^2\alpha x\,\mathrm{d}x = \frac{x^2}{4} - \frac{x\sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2} + C. \quad (2.37)$$

We shall also need the following result:

$$\int x\sin 2\alpha x\,\mathrm{d}x = -\frac{x\cos 2\alpha x}{2\alpha} + \frac{1}{2\alpha}\int \cos 2\alpha x\,\mathrm{d}x$$

therefore

$$\int x\sin 2\alpha x\,\mathrm{d}x = -\frac{x\cos 2\alpha x}{2\alpha} + \frac{\sin 2\alpha x}{4\alpha^2} + C. \quad (2.38)$$

For the derivation of the last integral formula needed we shall apply Eqns (2.37) and (2.38). We have already been well-trained in integration by parts so starting from

$$\int x^2 \sin^2 \alpha x \,\mathrm{d}x = \int x(x \sin^2 \alpha x)\,\mathrm{d}x$$

we obtain

$$\begin{aligned}\int x^2 \sin^2 \alpha x \,\mathrm{d}x = {} & x\left(\frac{x^2}{4} - \frac{x \sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2}\right) \\ & - \int \left(\frac{x^2}{4} - \frac{x \sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2}\right) \mathrm{d}x,\end{aligned}$$

that is,

$$\int x^2 \sin^2 \alpha x \,\mathrm{d}x = \frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^3}\right) \sin 2\alpha x - \frac{x \cos 2\alpha x}{4\alpha^2} + C.$$

Now a simple calculation gives

$$\langle x \rangle = \frac{2}{a} \int_0^a x \sin^2 \frac{n\pi x}{a} \mathrm{d}x = \frac{1}{2} a$$

and

$$\langle x^2 \rangle = \frac{2}{a} \int_0^a x^2 \sin^2 \frac{n\pi x}{a} \mathrm{d}x = \left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) a^2.$$

Notice that the right-hand side of the last equation is always positive and tends to $(1/3)a^2$ if $n \to \infty$. The last fact is a form of the very general "correspondence principle" [3, p. 317].

(b) Applying integration by parts ($\alpha \neq 0$, $\beta \neq 0$)

$$\int \sin \alpha x \sin \beta x \,\mathrm{d}x = -\frac{\cos \alpha x}{\alpha} \sin \beta x + \frac{\beta}{\alpha} \int \cos \alpha x \cos \beta x \,\mathrm{d}x$$

and

$$\int \sin \alpha x \sin \beta x \,\mathrm{d}x = -\frac{\cos \beta x}{\beta} \sin \alpha x + \frac{\alpha}{\beta} \int \cos \alpha x \cos \beta x \,\mathrm{d}x.$$

Expressing the common integral on the right-hand sides a rearrangement gives

$$\int \sin\alpha x \cos\beta x \,\mathrm{d}x = \frac{\beta \sin\alpha x \cos\beta x - \alpha \sin\beta x \cos\alpha x}{\alpha^2 - \beta^2}.$$

Using this formula for $i \neq j$ we find that

$$\frac{2}{a}\int_0^a \sin\frac{i\pi}{a}x \,\cos\frac{j\pi}{a}x \,\mathrm{d}x = 0$$

since the sine terms vanish. By the aid of a previously determined integral

$$\frac{2}{a}\int_0^a \sin^2\frac{n\pi}{a}x \,\mathrm{d}x = \frac{2}{a}\left[-\frac{\sin 2(n\pi/a)x}{4(n\pi/a)} + \frac{1}{2}x\right]_0^a = 1.$$

(c) Using again the already known integral of $\sin^2\alpha x$ we have

i.

$$\frac{2}{a}\int_0^{a/2} \sin^2\frac{\pi}{a}x \,\mathrm{d}x = \frac{1}{2}$$

ii.

$$\frac{2}{a}\int_0^{a/3} \sin^2\frac{2\pi}{a}x \,\mathrm{d}x = \frac{8\pi + 3\sqrt{3}}{24\pi} = 0.4022\ldots$$

iii.

$$\frac{2}{a}\int_{a/8}^{a/2} \sin^2\frac{3\pi}{a}x \,\mathrm{d}x = \frac{9\pi + 2\sqrt{2}}{24\pi} = 0.4125\ldots.$$

8. (a)

$$-\psi''(\xi)\psi(\xi) = 2c^2\xi^{2c-1} + c(1-c)\xi^{2c-2} - c(c+1)\xi^{2c},$$

$$\int_0^1 [-\psi''(\xi)\psi(\xi)]\,\mathrm{d}\xi = \frac{c}{(2c+1)(2c-1)},$$

$$\int_0^1 \psi^2(\xi)\,\mathrm{d}\xi = \frac{1}{(c+1)(2c+1)(2c+3)}.$$

On the basis of these formulas

$$\varepsilon(c) = \frac{c(c+1)(2c+3)}{(2c-1)}.$$

(b)

$$\varepsilon'(c) = \frac{f(c)}{(2c-1)^2},$$

where

$$f(c) = 8c^3 + 4c^2 - 10c - 3.$$

A local extremum can only occur at the value c_m that satisfies

$$f(c_\mathrm{m}) = 0.$$

According to the Descartes' rule of signs this equation has exactly one positive c_m solution, and, for example, $f(1) < 0$ and $f(2) > 0$ show that $1 < c_\mathrm{m} < 2$. The sign of the second derivative of the function ε at c_m is determined by the sign of

$$f'(c) = 24c^2 + 8c - 10 \tag{2.39}$$

at c_m. It is easy to see that in the interval $-\infty < c < \infty$ Eqn (2.39) describes a parabola opening upwards whose positive zero is 1/2. So $f'(c) > 0$ in the interval $c > 1/2$, and the function ε has a local minimum at c_m.

With an approximate equation solving method

$$c_\mathrm{m} = 1.0430\ldots,$$

and so

$$\frac{\varepsilon(c_\mathrm{m})}{\varepsilon_1} = 1.0111\ldots.$$

9. (a) First we derive the necessary integral formulas. We shall employ the integral

$$\int_0^\infty e^{-ax^2}\,\mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{a}}; \qquad a > 0,$$

which is usually taught in the basic mathematical courses for chemists. In the case of $a > 0$ and $n = 2, 3, 4$ we integrate the expression $x^{n-2}e^{-ax^2}$ by parts and obtain

$$\int_0^\infty x^{n-2}e^{-ax^2}\,\mathrm{d}x = \frac{2a}{n-1}\int_0^\infty x^n e^{-ax^2}\,\mathrm{d}x,$$

that is,

$$\int_0^\infty x^n e^{-ax^2}\,\mathrm{d}x = \frac{n-1}{2a}\int_0^\infty x^{n-2}e^{-ax^2}\,\mathrm{d}x. \tag{2.40}$$

If n is even, several applications of this formula yield

$$\int_0^\infty x^n e^{-ax^2}\mathrm{d}x = \frac{1\cdot 3\cdot 5\cdot\,\cdots\,\cdot(n-1)}{2^{(n/2)}a^{(n/2)}}\int_0^\infty x^0 e^{-ax^2}\,\mathrm{d}x,$$

that is,

$$\int_0^\infty x^n e^{-ax^2}\,\mathrm{d}x = \frac{1\cdot 3\cdot 5\cdot\,\cdots\,\cdot(n-1)}{2^{(n/2)+1}a^{(n+1)/2}}\sqrt{\pi}. \tag{2.41}$$

If n is odd, several applications of Eqn (2.40) leads to

$$\int_0^\infty x^n e^{-ax^2}\,\mathrm{d}x = \frac{2\cdot 4\cdot 6\cdot\,\cdots\,\cdot(n-1)}{2^{(n-1)/2}a^{(n-1)/2}}\int_0^\infty x^1 e^{-ax^2}\,\mathrm{d}x,$$

which, using

$$\int_0^\infty xe^{-ax^2}\,\mathrm{d}x = -\frac{1}{2a}\left[e^{-ax^2}\right]_0^\infty = \frac{1}{2a},$$

becomes

$$\int_0^\infty x^n e^{-ax^2}\,\mathrm{d}x = \frac{2\cdot 4\cdot 6\cdot\,\cdots\,\cdot(n-1)}{2^{(n+1)/2}a^{(n+1)/2}}. \tag{2.42}$$

The integrals having the lower limit $-\infty$ instead of 0 can be obtained from the equations above by simple symmetry considerations. Turning now to the particular problem

$$\begin{aligned}-\psi''(\xi)\psi(\xi)+\xi^2\psi^2(\xi) &= \big[-3c^2\xi^{10}+18c^2\xi^8-6c(2c+1)\xi^6\\ &\quad +20c\xi^4-3(4c+1)\xi^2+2\big]\,e^{-2\xi^2},\end{aligned}$$

$$\int_{-\infty}^\infty \left[-\psi''(\xi)\,\psi(\xi)+\xi^2\psi^2(\xi)\right]\,\mathrm{d}\,\xi = \frac{\sqrt{2\pi}(1845c^2-672c+1280)}{2048},$$

$$\int_{-\infty}^\infty \psi^2(\xi)\,\mathrm{d}\,\xi = \frac{\sqrt{2\pi}(105c^2+96c+256)}{512}.$$

Based on these formulas

$$\varepsilon(c) = \frac{1845c^2 - 672c + 1280}{4(105c^2 + 96c + 256)}.$$

It is easy to see that the denominator, a polynomial of second degree, cannot be zero for any real value of c.

(b)

$$\varepsilon'(c) = \frac{96f(c)}{(105c^2 + 96c + 256)^2},$$

where

$$f(c) = 645c^2 + 1760c - 768.$$

A local extremum is attained at c_m only if

$$f(c_\mathrm{m}) = 0.$$

This equation has two roots:

$$c_{\mathrm{m}1} = \frac{64\sqrt{310}}{645} - \frac{176}{129}; \qquad c_{\mathrm{m}2} = -\frac{64\sqrt{310}}{645} - \frac{176}{129}.$$

The sign of the second derivative of function ε at c_m is given by the sign of

$$f'(c) = 1290c + 1760$$

at c_m. It is easy to see that $f'(c_{\mathrm{m}1}) > 0$ and $f'(c_{\mathrm{m}2}) < 0$, so there is a local minimum at $c_{\mathrm{m}1}$ and a local maximum at $c_{\mathrm{m}2}$. The accuracy of the approximate energy is characterized by

$$\frac{\varepsilon(c_{\mathrm{m}1})}{\varepsilon_0} = \frac{13}{4} - \frac{\sqrt{310}}{8} = 1.0491\ldots.$$

10. (a) On the basis of the equation

$$\frac{\mathrm{d}E}{\mathrm{d}n}(n_\mathrm{m}) = h\nu_\mathrm{e}\left[1 - 2\left(n_\mathrm{m} + \frac{1}{2}\right)x_\mathrm{e}\right] = 0$$

there may be a unique local extremum at

$$n_{\mathrm{m}} = \frac{1}{2x_{\mathrm{e}}} - \frac{1}{2},$$

and, because of

$$\frac{\mathrm{d}^2E}{\mathrm{d}n^2}(n) = -2x_{\mathrm{e}} < 0,$$

this extremum is a local maximum. The value of the function E at n_{m}, that is, the dissociation energy is

$$D_{\mathrm{e}} = E(n_{\mathrm{m}}) = \frac{h\nu_{\mathrm{e}}}{4x_{\mathrm{e}}}.$$

(b)

$$D_{\mathrm{e}} = \frac{h\nu_{\mathrm{e}}}{4x_{\mathrm{e}}} = 8.537 \times 10^{-19}\,\mathrm{J}.$$

11. The first derivative is

$$\frac{\mathrm{d}f}{\mathrm{d}\lambda}(\lambda) = 8\pi hcf(\lambda)e^{-(hc/\lambda kT)},$$

where

$$f(\lambda) = \frac{1}{\lambda^7}\left(\frac{hc}{kT} - 5\lambda\right).$$

This derivative vanishes at

$$\lambda_{\mathrm{m}} = \frac{hc}{5kT}. \tag{2.43}$$

The sign of the second derivative at λ_{m} is determined by the sign of

$$\frac{\mathrm{d}f}{\mathrm{d}\lambda}(\lambda) = \frac{1}{\lambda^8}\left(30\lambda - \frac{7hc}{kT}\right)$$

at λ_{m}. Since

$$\frac{\mathrm{d}f}{\mathrm{d}\lambda}(\lambda_{\mathrm{m}}) = -\frac{hc}{kT\lambda_{\mathrm{m}}^8} < 0,$$

a local maximum appears at the point λ_{m}. A rearrangement of Eqn (2.43) yields

$$\lambda_{\mathrm{m}}T = \frac{hc}{5k},$$

and here the right-hand side really consists of fundamental physical constants.

12. (a) By the substitution $\lambda = \frac{hc}{kTx}$ we obtain

$$\frac{\mathrm{d}\lambda}{\mathrm{d}x} = -\frac{hc}{kTx^2}$$

and so

$$E = \int_0^\infty f(\lambda)\,\mathrm{d}\lambda = 8\pi hc\left(\frac{kT}{hc}\right)^4 \int_0^\infty \frac{x^3}{e^x - 1}\mathrm{d}x.$$

(b) Using Eqn (2.33)

$$\int_0^\infty x^3 e^{-x}\,\mathrm{d}x = \frac{3!}{1^4} = 6.$$

(c) By a simple transformation of the formula indicated

$$\int_0^\infty \frac{x^3}{e^x - 1}\mathrm{d}x = \int_0^\infty x^3 e^{-x} \sum_{k=0}^{\infty} e^{-kx}\,\mathrm{d}x.$$

Thus, applying again Eqn (2.33), the approximate integral is

$$I(n) = \int_0^\infty x^3 \sum_{k=0}^{n} e^{-(k+1)x}\,\mathrm{d}x = \sum_{k=0}^{n}\left(\int_0^\infty x^3 e^{-(k+1)x}\,\mathrm{d}x\right),$$

that is,

$$I(n) = 3!\sum_{k=0}^{n} \frac{1}{(k+1)^4}.$$

The case $n = 0$ corresponds to paragraph 12b, while

$$I(1) = 6.375; \qquad I(5) = 6.4867\ldots \text{ and } I(10) = 6.4926\ldots.$$

13. Silver (Ag): $C_{\mathrm{m}V}/\mathrm{J\,K^{-1}\,mol^{-1}} = 23.4322\ldots$; zinc (Zn): $C_{\mathrm{m}V}/\mathrm{J\,K^{-1}\,mol^{-1}} = 22.3467\ldots$; lead (Pb): $C_{\mathrm{m}V}/\mathrm{J\,K^{-1}\,mol^{-1}} = 24.6570\ldots$.

14. (a)

$$\frac{\mathrm{d}f}{\mathrm{d}v}(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} h(v)$$

where

$$h(v) = \left(2v - \frac{Mv^3}{RT}\right) e^{-(Mv^2/2RT)},$$

so, based on

$$h(v^*) = 0,$$

a local extremum can only occur at

$$v^* = \sqrt{\frac{2RT}{M}}.$$

Using the formulas

$$\frac{\mathrm{d}h}{\mathrm{d}v}(v) = e^{-(Mv^2/2RT)}\left(\frac{M^2v^4}{(RT)^2} - \frac{5Mv^2}{RT} + 2\right),$$

$$\frac{\mathrm{d}h}{\mathrm{d}v}(v^*) = -4e^{-1} < 0$$

there exists a local maximum at the point v^*.

(b)

$$v^* = 422\,\mathrm{m\,s^{-1}} = 1520\,\mathrm{km\,h^{-1}}$$

This speed can be compared to that of a jet airplane. However, the gas molecules fly towards a given direction for a short time only since they continuously collide with other gas molecules and the directions of their speeds change frequently.

(c) Using Eqns (2.41) and (2.42)

$$\langle v\rangle = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty v^3 e^{-Mv^2/2RT}\mathrm{d}v = \sqrt{\frac{8RT}{\pi M}}$$

$$\left\langle v^2\right\rangle = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty v^4 e^{-Mv^2/2RT}\mathrm{d}v = \frac{3RT}{M}.$$

15. Let

$$p_1(V_{\mathrm{m}}) = \frac{RT_{\mathrm{c}}}{V_{\mathrm{m}} - b} - \frac{a}{V_{\mathrm{m}}^2}.$$

At the critical point

$$p_{\mathrm{c}} = p_1(V_{\mathrm{mc}}) = \frac{RT_{\mathrm{c}}}{V_{\mathrm{mc}} - b} - \frac{a}{V_{\mathrm{mc}}^2},$$

moreover,

$$\frac{\mathrm{d}p_1}{\mathrm{d}V_{\mathrm{m}}}(V_{\mathrm{mc}}) = -\frac{RT_{\mathrm{c}}}{(V_{\mathrm{mc}} - b)^2} + \frac{2a}{V_{\mathrm{mc}}^3} = 0$$

and

$$\frac{\mathrm{d}^2p_1}{\mathrm{d}V_{\mathrm{m}}^2}(V_{\mathrm{mc}}) = \frac{2RT_{\mathrm{c}}}{(V_{\mathrm{mc}} - b)^3} - \frac{6a}{V_{\mathrm{mc}}^4} = 0.$$

From these three equations

$$p_{\mathrm{c}} = p_1(V_{\mathrm{mc}}) = \frac{a}{27b^2}; \qquad V_{\mathrm{mc}} = 3b; \qquad T_{\mathrm{c}} = \frac{8a}{27bR}.$$

16. Let x and y be the numerical values of T and ΔH, that is, let $x = T/\mathrm{K}$ and $y = \Delta H(\mathrm{J\,mol^{-1}})$, respectively. Then

(a)

$$\begin{aligned} y &= \int_{273}^{373} (27.83 + 4.19 \times 10^{-3}x)\,\mathrm{d}x \\ &= \left[27.83x + 4.19 \times 10^{-3}\frac{x^2}{2}\right]_{273}^{373} \\ &= 2918.337. \end{aligned}$$

(b)

$$\begin{aligned} y &= \left[28.29x + 2.53 \times 10^{-3}\frac{x^2}{2} - 5.44 \times 10^{-7}\frac{x^3}{3}\right]_{273}^{373} \\ &= 2904.9981\ldots. \end{aligned}$$

(c)

$$\begin{aligned} y &= \left[42.61x + 7.28 \times 10^{-3}\frac{x^2}{2} + 6.20 \times 10^{-5}x^{-1}\right]_{273}^{373} \\ &= 4496.1439\ \ldots. \end{aligned}$$

17. Let x and z be the numerical values of T and ΔS, that is, let $x = T/\mathrm{K}$ and $z = \Delta S/(\mathrm{J\,K^{-1}\,mol^{-1}})$, respectively. Then

(a)

$$\begin{aligned} z &= \int_{273}^{373} \left(\frac{27.83}{x} + 4.19 \times 10^{-3} \right) \mathrm{d}x \\ &= \left[27.83 \ln x + 4.19 \times 10^{-3} \right]_{273}^{373} \\ &= 8.8864 \ldots . \end{aligned}$$

(b)

$$\begin{aligned} z &= \left[28.29 \ln x + 2.53 \times 10^{-3} x - 5.44 \times 10^{-7} \frac{x^2}{2} \right]_{273}^{373} \\ &= 9.0649 \ldots . \end{aligned}$$

(c)

$$\begin{aligned} z &= \left[42.61 \ln x + 7.28 \times 10^{-3} x + 6.20 \times 10^{-5} \frac{x^{-2}}{2} \right]_{273}^{373} \\ &= 14.0268 \ldots . \end{aligned}$$

18. (a) From the formula of the path and Eqn (1.31)

$$\hat{V}^{\alpha+1}(T) = \frac{nRT}{a},$$

which yields

$$\frac{\mathrm{d}\hat{V}}{\mathrm{d}T}(T) = \frac{nR}{(\alpha+1)a} \hat{V}^{-\alpha}(T)$$

and, after some calculation,

$$C = C_V + \frac{nR}{\alpha+1}.$$

(b) Now we cannot give the function $\hat{V}$ directly. However, the derivative of the function defined by

$$\hat{T}(V) = p_0 \frac{V \ln\left(1 + \frac{V}{V_0}\right)}{nR} \tag{2.44}$$

is

$$\frac{\mathrm{d}\hat{T}}{\mathrm{d}V}(V) = \frac{p_0}{nR}\left[\ln\left(1+\frac{V}{V_0}\right) + \frac{V}{V_0\left(1+\frac{V}{V_0}\right)}\right] > 0,$$

and $\hat{T}(V) \to 0$ if $V \to 0$. This means that the inverse of $\hat{T}$ is defined for any $T > 0$, it is differentiable and

$$\frac{\mathrm{d}\hat{V}}{\mathrm{d}T}(T) = \frac{1}{(\mathrm{d}\hat{T}/\mathrm{d}V)(\hat{V}(T))}.$$

Thus,

$$C(T) = C_V(T) + \frac{nR\ln\left[1+\frac{\hat{V}(T)}{V_0}\right]}{\ln\left[1+\frac{\hat{V}(T)}{V_0}\right] + \frac{\hat{V}(T)}{V_0\left[1+\frac{\hat{V}(T)}{V_0}\right]}}.$$

19. (a)

$$\begin{aligned}\frac{\partial H}{\partial T}(p,T) &= \frac{\partial U}{\partial T}(\hat{V}(p,T),T) + \frac{\partial U}{\partial V}(\hat{V}(p,T),T)\frac{\partial \hat{V}}{\partial T}(p,T)\\ &\quad + p\frac{\partial \hat{V}}{\partial T}(p,T),\\ \frac{\partial H}{\partial T}(p,T) &= \frac{\partial U}{\partial T}(\hat{V}(p,T),T) + \left[\frac{\partial U}{\partial V}(\hat{V}(p,T),T) + p\right]\frac{\partial \hat{V}}{\partial T}(p,T);\end{aligned}$$

(b)

$$\begin{aligned}\frac{\partial U}{\partial T}(V,T) &= \frac{\partial H}{\partial T}(\hat{p}(V,T),T) + \frac{\partial H}{\partial p}(\hat{p}(V,T),T)\frac{\partial \hat{p}}{\partial T}(V,T)\\ &\quad - \frac{\partial \hat{p}}{\partial T}(V,T)V,\\ \frac{\partial U}{\partial T}(V,T) &= \frac{\partial H}{\partial T}(\hat{p}(V,T),T) + \left[\frac{\partial H}{\partial p}(\hat{p}(V,T),T) - V\right]\frac{\partial \hat{p}}{\partial T}(V,T).\end{aligned}$$

20. By virtue of the equation

$$g(V,T) = f(\hat{p}(V,T),V,T) = 0$$

g is independent of volume V, so

$$\begin{aligned}\frac{\partial g}{\partial V}(V,T) &= \frac{\partial f}{\partial V}(\hat{p}(V,T),V,T) + \frac{\partial f}{\partial p}(\hat{p}(V,T),V,T)\frac{\partial \hat{p}}{\partial V}(V,T)\\ &= 0,\end{aligned}$$

that is,

$$\frac{\partial \hat{p}}{\partial V}(V,T) = -\frac{(\partial f/\partial V)(\hat{p}(V,T),V,T)}{(\partial f/\partial p)(\hat{p}(V,T),V,T)}. \tag{2.45}$$

Similar considerations yield

$$\frac{\partial \hat{V}}{\partial T}(p,T) = -\frac{(\partial f/\partial T)(p,\hat{V}(p,T),T)}{(\partial f/\partial V)(p,\hat{V}(p,T),T)} \tag{2.46}$$

furthermore

$$\frac{\partial \hat{T}}{\partial p}(p,V) = -\frac{(\partial f/\partial p)(p,V,\hat{T}(p,V))}{(\partial f/\partial T)(p,V,\hat{T}(p,V))}. \tag{2.47}$$

For the triples (p,V,T) satisfying the equation $f(p,V,T)=0$ the formulas $\hat{p}(V,T)=p$, $\hat{V}(p,T)=V$ and $\hat{T}(p,V)=T$ are also valid. If we insert these three function values into Eqns (2.45)–(2.47), and multiply the latters with each other we obtain the statement to be proved.

21. The function to be investigated is defined as

$$f([\mathrm{H}^+]) = [\mathrm{H}^+] + \frac{K_\mathrm{w}}{[\mathrm{H}^+]}; \qquad [\mathrm{H}^+] > 0.$$

The existence of at least one local minimum can already be inferred from the expression

$$\lim_{[\mathrm{H}^+]\to 0} f([\mathrm{H}^+]) = \lim_{[\mathrm{H}^+]\to\infty} f([\mathrm{H}^+]) = \infty.$$

Differentiating

$$\frac{\mathrm{d}f}{\mathrm{d}[\mathrm{H}^+]}([\mathrm{H}^+]) = 1 - \frac{K_\mathrm{w}}{[\mathrm{H}^+]^2},$$

which vanishes at

$$[\mathrm{H}^+]_\mathrm{m} = \sqrt{K_\mathrm{w}}.$$

Because of

$$\frac{d^2 f}{d[H^+]^2}([H^+]) = \frac{2K_w}{[H^+]^3} > 0$$

there exists a local minimum at $[H^+]_m$. Here $[OH^-]_m = K_w/[H^+]_m = [H^+]_m$.

22. (a) After some algebraic manipulation

$$[A^{\pm}]([H^+]) = \frac{K_1 A [H^+]}{[H^+]^2 + K_1[H^+] + K_1 K_2}.$$

Differentiating the function just obtained

$$\frac{d[A^{\pm}]}{d[H^+]}([H^+]) = \frac{K_1 A f([H^+])}{([H^+]^2 + K_1[H^+] + K_1 K_2)^2},$$

where

$$f([H^+]) = K_1 K_2 - [H^+]^2.$$

From $f([H^+]_m) = 0$

$$[H^+]_m = \sqrt{K_1 K_2}, \tag{2.48}$$

and this is the only point at which a local extremum can occur. The sign of the second derivative of $[A^{\pm}]$ at $[H^+]_m$ depends on the sign of $f'([H^+]_m)$ so, according to

$$f'([H^+]_m) = -2\sqrt{K_1 K_2} < 0,$$

a local maximum is exhibited at $[H^+]_m$.

(b) From the formulas given in the problem we obtain $[A^+]_m = [A^-]_m$ at $[H^+]_m$. Thus, at $[H^+]_m$ the numbers of the negatively and positively charged ions formed from the amino acid are equal to each other, and the “isoelectric point” briefly refers to this state.

23. (a) The derivative of the function in question is

$$f'(x) = \frac{s(x)}{p^2(x)},$$

where

$$s(x) = \left[p'(x) + xp''(x)\right]p(x) - xp'^2(x).$$

Using the formulas

$$p(x) = \sum_{i=0}^{n} a_i x^i,$$

$$p'(x) = \sum_{i=0}^{n} i a_i x^{i-1}$$

and

$$p''(x) = \sum_{i=0}^{n} i(i-1) a_i x^{i-2}$$

we can write that

$$s(x) = \frac{1}{x} \sum_{i=0}^{n} \sum_{j=0}^{n} (i^2 - ij) a_i\, a_j\, x^i\, x^j,$$

and

$$s(x) = \frac{1}{2x} \left[\sum_{i=0}^{n} \sum_{j=0}^{n} (i^2 - ij) a_i a_j x^i x^j \right. \\ \left. + \sum_{i=0}^{n} \sum_{j=0}^{n} (j^2 - ij) a_i a_j x^i x^j \right],$$

from which it follows that

$$s(x) = \frac{1}{2x} \sum_{i=0}^{n} \sum_{j=0}^{n} (i-j)^2 a_i a_j x^i x^j > 0,$$

if $x > 0$. So $f'(x) > 0$, if $x > 0$, which means that f is a strictly monotonously increasing function in the interval $(0, \infty)$ (in [40] an other proof can be found).

(b) In the following let x be always positive. The first function on the right-hand side of Eqn (1.34) is strictly monotonously decreasing. The terms of the sum of positive sign are strictly monotonously increasing functions of $1/x$ so they are strictly monotonously decreasing functions of x. Finally, the terms of the sum of negative sign are strictly monotonously increasing functions of x. Thus, the right-hand side of Eqn (1.34) is a strictly monotonously decreasing function of x, while the left-hand side increases strictly monotonously with x. The curve of a strictly monotonously increasing function clearly can cross the curve of a strictly monotonously decreasing function only once. So Eqn (1.34) can have at most one positive root [40].

24. (a)

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{L}]}([\mathrm{L}]) = -\frac{T_{\mathrm{M}}(\sum_{j=1}^{n} j\beta_j[\mathrm{L}]^{j-1})}{(1+\sum_{j=1}^{n}\beta_j[\mathrm{L}]^j)^2} < 0,$$

so [M] strictly monotonously decreases with [L].

(b)

$$\frac{\mathrm{d}[\mathrm{ML}_i]}{\mathrm{d}[\mathrm{L}]}([\mathrm{L}]) = T_{\mathrm{M}}\beta_i\frac{[\mathrm{L}]^{i-1}f([\mathrm{L}])}{(1+\sum_{j=1}^{n}\beta_j[\mathrm{L}]^j)^2}, \tag{2.49}$$

where

$$f([\mathrm{L}]) = i + \sum_{j=1}^{n}(i-j)\beta_j[\mathrm{L}]^j. \tag{2.50}$$

Thus, local extrema can occur at the values $[\mathrm{L}]_{\mathrm{m}}$ satisfying

$$f([\mathrm{L}]_{\mathrm{m}}) = 0. \tag{2.51}$$

The left-hand side of this equation is a polynomial whose coefficients are positive for $j < i$ and – provided $i < n$ – negative for $j > i$. There will be only one sign change in the sequence of the coefficients, which means only one positive real root $[\mathrm{L}]_{\mathrm{m}}$ according to the Descartes' rule of signs. Since $f([\mathrm{L}]) \to i > 0$, if $[\mathrm{L}] \to 0$ and – because of the negative coefficient of the term of highest degree – $f([\mathrm{L}]) \to -\infty$, if $[\mathrm{L}] \to \infty$, it follows that at $[\mathrm{L}]_{\mathrm{m}}$ f changes its sign in the direction positive → negative. Equation (2.49) undergoes the same sign change at $[\mathrm{L}]_{\mathrm{m}}$, so the function $[\mathrm{ML}_i]$ has a local maximum at $[\mathrm{L}]_{\mathrm{m}}$.

Eqn (2.51) can be transformed into

$$i\left(1+\sum_{j=1}^{n}\beta_j[\mathrm{L}]_{\mathrm{m}}^j\right) = \sum_{j=1}^{n} j\beta_j[\mathrm{L}]_{\mathrm{m}}^j,$$

from which the expression needed follows evidently.

(c) Let $i = n$, and apply the considerations corresponding to paragraph 24b. Since now $f([\mathrm{L}]) > 0$ for arbitrary values of [L], the first derivative of the function $[\mathrm{ML}_i]$ is positive everywhere, and the function itself is strictly monotonously increasing.

25.

$$\frac{\mathrm{d}x_\mathrm{C}}{\mathrm{d}\xi}(\xi) = \frac{f(\xi)}{[1+\xi-x(\xi)]^2},$$

where

$$f(\xi) = \frac{\mathrm{d}x}{\mathrm{d}\xi}(\xi)(1+\xi) - x(\xi),$$

and

$$\frac{\mathrm{d}x}{\mathrm{d}\xi}(\xi) = \frac{1}{2}\left[1 - \frac{(1+K)\xi + 1 - K}{\sqrt{1+K}\sqrt{(1+\xi)^2 + K(1-\xi)^2}}\right].$$

A local extremum can only occur at a value ξ_m that satisfies

$$f(\xi_\mathrm{m}) = 0.$$

Combining the previous equations we obtain the value

$$\xi_\mathrm{m} = 1.$$

This corresponds to the stoichiometric ratio of the reactants, but we must still demonstrate that there exist a local maximum at ξ_m. The sign of the second derivative of the function x_C at ξ_m is determined by the sign of the expression

$$\frac{\mathrm{d}f}{\mathrm{d}\xi}(\xi) = (1+\xi)\frac{\mathrm{d}^2x}{\mathrm{d}\xi^2}(\xi)$$

at ξ_m. Thus, the actual problem is to reveal the sign of the second derivative on the right-hand side at ξ_m. After differentiation and some calculation

$$\frac{\mathrm{d}^2x}{\mathrm{d}\xi^2}(\xi) = -\frac{2K}{\sqrt{1+K}\left[(1+\xi)^2 + K(1-\xi)^2\right]^{3/2}} < 0,$$

so there is a local maximum at each point where the first derivative of x_C vanishes. Thus, x_C exhibits a local maximum at the point ξ_m.

26. In the condition $b_0 = c_0 = 0$

(a)

$$\frac{\mathrm{d}b}{\mathrm{d}t}(t) = \frac{a_0 k_1 (k_1 e^{-k_1 t} - k_2 e^{-k_2 t})}{k_1 - k_2},$$

which, according to

$$k_1 e^{-k_1 t_\mathrm{m}} - k_2 e^{-k_2 t_\mathrm{m}} = 0, \tag{2.52}$$

vanishes at

$$t_\mathrm{m} = \frac{\ln(k_2/k_1)}{k_2 - k_1} > 0.$$

Using Eqn (2.52) the second derivative

$$\frac{\mathrm{d}^2 b}{\mathrm{d}t^2}(t) = \frac{k_1 a_0 (k_2^2 e^{-k_2 t} - k_1^2 e^{-k_1 t})}{k_1 - k_2}$$

at the point t_m will assume the value

$$\frac{\mathrm{d}^2 b}{\mathrm{d}t^2}(t_\mathrm{m}) = -k_1 k_2 a_0 e^{-k_2 t_\mathrm{m}} = -k_1^2 a_0 e^{-k_1 t_\mathrm{m}} < 0,$$

so a local maximum occurs at t_m.

(b) Differentiating we find

$$\frac{\mathrm{d}c}{\mathrm{d}t}(t) = \frac{k_1 k_2 a_0 (e^{-k_2 t} - e^{-k_1 t})}{k_1 - k_2}$$

and

$$\frac{\mathrm{d}^2 c}{\mathrm{d}t^2}(t) = \frac{k_1 k_2 a_0 (k_1 e^{-k_1 t} - k_2 e^{-k_2 t})}{k_1 - k_2}.$$

According to

$$k_1 e^{-k_1 t_\mathrm{i}} - k_2 e^{-k_2 t_\mathrm{i}} = 0$$

the second derivative vanishes at

$$t_\mathrm{i} = \frac{\ln(k_2/k_1)}{k_2 - k_1} > 0,$$

so this is the point at which an inflection point can occur. Notice that $t_\mathrm{i} = t_\mathrm{m}$. If the second derivative of c changes its sign at t_i then an inflection point has to occur there [30, p. 431]. This latter condition, however, is fulfilled since the derivative of the function f defined by

$$f(t) = k_1 e^{-k_1 t} - k_2 e^{-k_2 t}$$

is

$$f'(t_\mathrm{i}) = -k_1^2 e^{-k_1 t_\mathrm{i}} + k_2^2 e^{-k_2 t_\mathrm{i}} = -k_2 e^{-k_2 t_\mathrm{i}}(k_1 - k_2)$$

at t_i, so f is locally increasing at t_i if $k_1 - k_2 < 0$ and is locally decreasing if $k_1 - k_2 > 0$.

27. (a)

$$v(t) = ka(t)b(t) = ka_0 b_0 (a_0 + b_0)^2 \frac{e^{(a_0+b_0)kt}}{\left[b_0 e^{(a_0+b_0)kt} + a_0\right]^2}$$

$$\frac{\mathrm{d}v}{\mathrm{d}t}(t) = \frac{a_0 b_0 (a_0 + b_0)^3 k^2 f(t)}{\left[b_0 e^{(a_0+b_0)kt} + a_0\right]^3 e^{-(a_0+b_0)kt}},$$

where

$$f(t) = a_0 - b_0 e^{(a_0+b_0)kt}.$$

Thus, according to

$$f(t_\mathrm{m}) = 0,$$

a local extremum can only occur at the point

$$t_\mathrm{m} = \frac{1}{k(a_0 + b_0)} \ln\left(\frac{a_0}{b_0}\right) > 0.$$

The sign of the second derivative of function v with respect to t at t_m is determined by the expression

$$\frac{\mathrm{d}f}{\mathrm{d}t}(t_\mathrm{m}) = -b_0(a_0 + b_0)k e^{(a_0+b_0)kt_\mathrm{m}} < 0.$$

This means that a local maximum occurs at t_m.

(b)

$$\frac{\mathrm{d}a}{\mathrm{d}t}(t) = -\frac{a_0 b_0 (a_0 + b_0)^2 k e^{(a_0+b_0)kt}}{\left[b_0 e^{(a_0+b_0)kt} + a_0\right]^2} < 0,$$

from which it follows that the function a strictly monotonously decreases in its entire interval of definition. As the formula

$$\frac{\mathrm{d}^2 a}{\mathrm{d}t^2}(t) = -\frac{a_0 b_0 (a_0 + b_0)^3 k^2 f(t)}{\left[b_0 e^{(a_0+b_0)kt} + a_0\right]^3 e^{-(a_0+b_0)kt}}$$

for the second derivative shows, the second derivative changes its sign at the t_{m} value above. This means that at t_{m} the curve of the function a goes from one side of the tangent line at t_{m} to the other, that is, a has an inflection point at t_{m} [30, p. 431]. Since

$$a(t) + b(t) = a_0 + b_0$$

and so

$$\frac{\mathrm{d}^2 b}{\mathrm{d}t^2}(t) = -\frac{\mathrm{d}^2 a}{dt^2}(t),$$

the function b also has an inflection point at t_{m}.

28. (a) The necessary derivatives are as follows:

$$\frac{\partial c}{\partial x}(x,t) = -\frac{c_0 x}{4\sqrt{\pi D^3 t^3}} e^{-(x^2/4Dt)},$$

$$\frac{\partial^2 c}{\partial x^2}(x,t) = \frac{c_0 (x^2 - 2Dt)}{8\sqrt{\pi D^5 t^5}} e^{-(x^2/4Dt)}$$

and

$$\frac{\partial c}{\partial t}(x,t) = \frac{c_0 (x^2 - 2Dt)}{8\sqrt{\pi D^3 t^5}} e^{-(x^2/4Dt)}. \tag{2.53}$$

Thus,

$$\frac{\partial c}{\partial t}(x,t) = D\frac{\partial^2 c}{\partial x^2}(x,t)$$

for $t > 0$ and $-\infty < x < \infty$.

(b) Applying Eqn (2.53) we obtain

$$\frac{\mathrm{d}f}{\mathrm{d}t}(t) = \frac{c_0}{8\sqrt{\pi D^3}} g(t) e^{-(x_0^2/4Dt)},$$

where

$$g(t) = \frac{x_0^2 - 2Dt}{\sqrt{t^5}}.$$

The first derivative of f becomes zero at the point

$$t_{\rm m} = \frac{x_0^2}{2D}. \tag{2.54}$$

Since the sign of $(\mathrm{d}^2 f/\mathrm{d}t^2)(t_{\rm m})$ agrees with that of $(dg/dt)(t_{\rm m})$, it follows from

$$\frac{\mathrm{d}g}{\mathrm{d}t}(t_{\rm m}) = -\frac{2D}{\sqrt{t_{\rm m}^5}} < 0$$

that there is a local maximum at $t_{\rm m}$. For the determination of the diffusion coefficient D we measure the temporal change of the concentration c at an accurately known coordinate x_0, and determine the time moment $t_{\rm m}$ belonging to the local maximum of the concentration *vs*. time curve. After this we calculate the value of D from Eqn (2.54).

29. From the equation

$$b(x_{\rm c}(t), t) = \frac{b_0 e^{(p-m)g(a_0)t} e^{-(x_{\rm c}^2(t)/4Dt)}}{\sqrt{4\pi Dt}} = b_{\rm c}$$

we have

$$x_{\rm c}(t) = \pm\sqrt{2D}\sqrt{t \ln\left(\frac{b_0^2}{4\pi D b_{\rm c}^2 t}\right) + 2(p-m)g(a_0)t^2},$$

and differentiating with respect to t

$$\frac{\mathrm{d}x_{\rm c}}{\mathrm{d}t}(t) = \mp\sqrt{2D}\frac{\left[\ln\left(\frac{4\pi D b_{\rm c}^2 t}{b_0^2}\right) - 4(p-m)g(a_0)t + 1\right]}{\sqrt{4t\ln\left(\frac{b_0^2}{4\pi D b_{\rm c}^2 t}\right) + 8(p-m)g(a_0)t^2}}.$$

30. (a) According to Fig. 1.1

$$\sin\alpha(x) = \frac{x}{\sqrt{x^2 + a^2}}$$

and

$$\sin \beta(x) = \frac{(c-x)}{\sqrt{(c-x)^2+b^2}}.$$

Differentiating the function T we obtain

$$T'(x) = \frac{x}{v_1\sqrt{x^2+a^2}} - \frac{(c-x)}{v_2\sqrt{(c-x)^2+b^2}}$$

which can be written as

$$T'(x) = \frac{\sin \alpha(x)}{v_1} - \frac{\sin \beta(x)}{v_2}.$$

Now it is easy to see that $T'(x_{\mathrm{m}}) = 0$ implies

$$\frac{\sin \alpha(x_{\mathrm{m}})}{\sin \beta(x_{\mathrm{m}})} = \frac{v_1}{v_2}.$$

The second derivative of T,

$$\begin{aligned} T''(x) = {} & \frac{a^2}{v_1(x^2+a^2)\sqrt{x^2+a^2}} \\ & + \frac{b^2}{v_2\left[(c-x)^2+b^2\right]\sqrt{(c-x)^2+b^2}}, \end{aligned}$$

is obviously positive on the whole domain of definition.

(b) Simple considerations show that

$$\lim_{x\to 0} T'(x) = -\frac{c}{v_2\sqrt{b^2+c^2}} < 0$$

and

$$\lim_{x\to c} T'(x) = \frac{c}{v_1\sqrt{a^2+c^2}} > 0.$$

The signs of these limits and the continuity of T' ensure that T' has at least one zero. Since T' is strictly increasing (cf. $T''(x) > 0$), it cannot have more than one zero.

31. (a) There exists cross-inhibition since

$$\frac{\partial f_1}{\partial c_2}(c_1, c_2) = -k_2 c_1 < 0$$

for any $(c_1, c_2) \in \mathbb{R}^2_+$.

(b) There exists cross-inhibition since

$$\frac{\partial f_1}{\partial c_2}(c_1, c_2, c_3) = -2c_1c_2 + 3\eta_1 c_2^2 < 0$$

is valid for the points $(c_1, c_2, c_3) \in \mathbb{R}_+^3$ with

$$c_1 > \frac{3}{2}\eta_1 c_2.$$

(c) Cross-inhibition is present since

$$\frac{\partial f_3}{\partial c_2}(c_1, c_2, c_3) = \frac{a_{10}(1 - a_9c_2^2)}{(1 + c_2 + a_9c_2^2)^2(1 + c_3)} < 0$$

for the points $(c_1, c_2, c_3) \in \mathbb{R}_+^3$ with

$$c_2^2 > \frac{1}{a_9}.$$

(d)

$$\frac{\partial f_i}{\partial c_l}(c_1, c_2, \dots, c_n) = k_{il} \geq 0 \quad \text{if } i \neq l,$$

so there is no cross-inhibition for any $(c_1, c_2, \dots, c_n) \in \mathbb{R}_+^n$, either.
Turing instability [89], a diffusion-driven pattern forming mechanism, has been found experimentally in some chemical systems [90, p. 299], and can be related to a number of biological phenomena [14]. For a class of rate equations Szili and Tóth [45, 46] have shown that the presence of cross-inhibition at the homogeneous stationary state of the system is a necessary condition of Turing instability.

32. The first derivative of f is

$$f'(c) = -2\sum_{i=1}^{n}(c_i - c),$$

hence a local extremum at c^* implies

$$\sum_{i=1}^{n}(c_i - c^*) = \sum_{i=1}^{n} c_i - nc^* = 0$$

that is,

$$c^* = \frac{\sum_{i=1}^{n} c_i}{n}. \tag{2.55}$$

The second derivative of f is

$$f''(c) = 2n > 0,$$

which means that there exists a local minimum at the value c^* given by Eqn (2.55).

33. The first derivative of f is

$$f'(x) = -2\sum_{i=1}^{n} c_i(A_i - c_i x),$$

so if there exists a local extremum at x^* then

$$\sum_{i=1}^{n} c_i(A_i - c_i x^*) = 0,$$

which yields

$$x^* = \frac{\sum_{i=1}^{n} A_i c_i}{\sum_{i=1}^{n} c_i^2}. \tag{2.56}$$

The second derivative of f is given by

$$f''(x) = 2\sum_{i=1}^{n} c_i^2 > 0,$$

which implies the existence of a local minimum at the value x^* given by Eqn (2.56).

34. Differentiating f we obtain

$$\begin{aligned}
\frac{\partial f}{\partial x}(x,y) &= 2\sum_{i=1}^{n}(x - y\sqrt{c_i} - \Lambda_{\mathrm{m}i}),\\
\frac{\partial f}{\partial y}(x,y) &= -2\sum_{i=1}^{n}(x - y\sqrt{c_i} - \Lambda_{\mathrm{m}i})\sqrt{c_i},\\
\frac{\partial^2 f}{\partial x^2}(x,y) &= 2n > 0,\\
\frac{\partial^2 f}{\partial y^2}(x,y) &= 2\sum_{i=1}^{n} c_i
\end{aligned}$$

and

$$\frac{\partial^2 f}{\partial y \partial x}(x, y) = -2\sum_{i=1}^{n}\sqrt{c_i}.$$

If the function f has a local extremum at (x^*, y^*) then

$$\frac{\partial f}{\partial x}(x^*, y^*) = \frac{\partial f}{\partial y}(x^*, y^*) = 0,$$

which leads to the linear system

$$\begin{aligned} nx^* - \left(\textstyle\sum_{i=1}^{n}\sqrt{c_i}\right)y^* &= \textstyle\sum_{i=1}^{n}\Lambda_{\mathrm{m}i}, \\ \left(\textstyle\sum_{i=1}^{n}\sqrt{c_i}\right)x^* - \left(\textstyle\sum_{i=1}^{n}c_i\right)y^* &= \textstyle\sum_{i=1}^{n}\Lambda_{\mathrm{m}i}\sqrt{c_i}. \end{aligned} \tag{2.57}$$

The value of the determinant of this system can be written as

$$\begin{aligned} D = -n\sum_{i=1}^{n}c_i + \left(\sum_{i=1}^{n}\sqrt{c_i}\right)^2 &= -n\left[\sum_{i=1}^{n}c_i - n\left(\frac{1}{n}\sum_{i=1}^{n}\sqrt{c_i}\right)^2\right] \\ &= -n\left[\sum_{i=1}^{n}c_i - n\left(\overline{\sqrt{c_i}}\right)^2\right] \\ &= -n\sum_{i=1}^{n}\left[\sqrt{c_i} - \overline{\sqrt{c_i}}\right]^2, \end{aligned}$$

which can be zero only in the degenerate case $c_1 = c_2 = \cdots = c_n$. Since the latter relationship is excluded, Eqn (2.57) has exactly one solution (x^*, y^*), which can be routinely expressed from the corresponding equations. At the point (x^*, y^*) a local minimum occurs since

$$\frac{\partial^2 f}{\partial x^2}(x^*, y^*) = 2n > 0$$

and

$$\frac{\partial^2 f}{\partial x^2}(x^*, y^*)\frac{\partial^2 f}{\partial y^2}(x^*, y^*) - \left[\frac{\partial^2 f}{\partial y \partial x}(x^*, y^*)\right]^2 = -4D > 0.$$

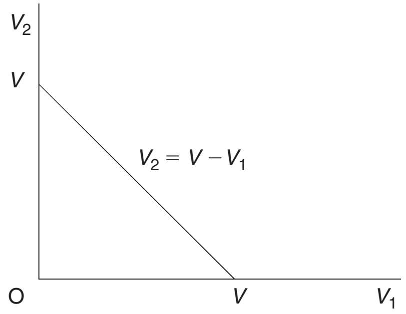


Figure 2.7 The domain of definition of $\hat{n}$ is the inside of the triangle VOV below the straight line $V_2 = V - V_1$

35. (a) Taking into account that $V_3 > 0$, the domain of definition of the function $\hat{n}$ defined by

$$\hat{n}(V_1, V_2) = n(V_1, V_2, V - V_1 - V_2) \tag{2.58}$$

is the set $\{(V_1, V_2) | V - V_1 - V_2 > 0\}$. The graphical picture of this set can be seen in Fig. 2.7. The necessary condition of a local extremum is

$$\frac{\partial \hat{n}}{\partial V_1}(\overline{V}_1, \overline{V}_2) = 0; \qquad \frac{\partial \hat{n}}{\partial V_2}(\overline{V}_1, \overline{V}_2) = 0,$$

from which we obtain

$$V - 2\overline{V}_1 - \overline{V}_2 = 0; \qquad V - \overline{V}_1 - 2\overline{V}_2 = 0,$$

that is,

$$\overline{V}_1 = \overline{V}_2 = \frac{1}{3}V.$$

To investigate whether the sufficient condition of the existence of a local extremum is fulfilled we calculate the following quantities:

$$a_{11} = \frac{\partial^2 \hat{n}}{\partial V_1^2}\left(\frac{1}{3}V, \frac{1}{3}V\right) = -\frac{486K^3 c_A V_A^4}{(3KV_A + V)^5} < 0,$$

$$a_{22} = \frac{\partial^2 \hat{n}}{\partial V_2^2}\left(\frac{1}{3}V, \frac{1}{3}V\right) = -\frac{486K^3 c_A V_A^4}{(3KV_A + V)^5} < 0$$

and

$$a_{12} = \frac{\partial^2 \hat{n}}{\partial V_2 \partial V_1}\left(\frac{1}{3}V, \frac{1}{3}V\right) = -\frac{243K^3 c_{\mathrm{A}} V_{\mathrm{A}}^4}{(3KV_{\mathrm{A}} + V)^5} < 0.$$

Since $a_{11} < 0$ and

$$a_{11}a_{22} - a_{12}^2 = \frac{177147K^6 c_{\mathrm{A}}^2 V_{\mathrm{A}}^8}{(3KV_{\mathrm{A}} + V)^{10}} > 0,$$

a local maximum occurs at the point $(\frac{1}{3}V, \frac{1}{3}V)$. With

$$\overline{V}_3 = V - \overline{V}_1 - \overline{V}_2 = \frac{1}{3}V$$

we have proved that the maximal amount of the solute can be extracted if we use the same volume of the extracting solvent in each of the three cases.

(b) If the function x has a local extremum at the point $(\overline{V}_1, \overline{V}_2, \overline{V}_3)$ then, according to the method of Lagrange multipliers [30, p. 482], there exists exactly one quantity λ for which the derivatives of the function φ defined by

$$\varphi(V_1, V_2, V_3) = n(V_1, V_2, V_3) + \lambda(V - V_1 - V_2 - V_3)$$

satisfy the system of equations

$$\begin{aligned}
\frac{\partial \varphi}{\partial V_1}(\overline{V}_1, \overline{V}_2, \overline{V}_3) &= \frac{\partial n}{\partial V_1}(\overline{V}_1, \overline{V}_2, \overline{V}_3) - \lambda = 0\\
\frac{\partial \varphi}{\partial V_2}(\overline{V}_1, \overline{V}_2, \overline{V}_3) &= \frac{\partial n}{\partial V_2}(\overline{V}_1, \overline{V}_2, \overline{V}_3) - \lambda = 0\\
\frac{\partial \varphi}{\partial V_3}(\overline{V}_1, \overline{V}_2, \overline{V}_3) &= \frac{\partial n}{\partial V_3}(\overline{V}_1, \overline{V}_2, \overline{V}_3) - \lambda = 0\\
V - \overline{V}_1 - \overline{V}_2 - \overline{V}_3 &= 0.
\end{aligned}$$

Thus, the possible local extrema can be found by solving this system of equations. If $(\overline{V}_1, \overline{V}_2, \overline{V}_3, \lambda)$ is a solution then $(\overline{V}_1, \overline{V}_2, \overline{V}_3)$ satisfies the system

$$\begin{aligned}\frac{\partial n}{\partial V_1}(\overline{V}_1,\overline{V}_2,\overline{V}_3)-\frac{\partial n}{\partial V_3}(\overline{V}_1,\overline{V}_2,\overline{V}_3)&=0\\ \frac{\partial n}{\partial V_2}(\overline{V}_1,\overline{V}_2,\overline{V}_3)-\frac{\partial n}{\partial V_3}(\overline{V}_1,\overline{V}_2,\overline{V}_3)&=0\\ V-\overline{V}_1-\overline{V}_2-\overline{V}_3&=0,\end{aligned}$$

and, because of

$$\begin{aligned}\frac{\partial \hat{n}}{\partial V_1}(V_1,V_2)&=\frac{\partial}{\partial V_1}\left[n(V_1,V_2,V-V_1-V_2)\right],\\ \frac{\partial \hat{n}}{\partial V_1}(V_1,V_2)&=\frac{\partial n}{\partial V_1}(V_1,V_2,V_3)-\frac{\partial n}{\partial V_3}(V_1,V_2,V_3),\\ \frac{\partial \hat{n}}{\partial V_2}(V_1,V_2)&=\frac{\partial}{\partial V_2}\left[n(V_1,V_2,V-V_1-V_2)\right],\\ \frac{\partial \hat{n}}{\partial V_2}(V_1,V_2)&=\frac{\partial n}{\partial V_2}(V_1,V_2,V_3)-\frac{\partial n}{\partial V_3}(V_1,V_2,V_3),\\ V_3&=V-V_1-V_2,\end{aligned}$$

it also satisfies the system

$$\begin{gathered}\frac{\partial \hat{n}}{\partial V_1}(\overline{V}_1,\overline{V}_2)=0;\qquad \frac{\partial \hat{n}}{\partial V_2}(\overline{V}_1,\overline{V}_2)=0,\\ \overline{V}_3=V-\overline{V}_1-\overline{V}_2.\end{gathered}$$

It follows from the previous considerations that this system has the unique solution $(\frac{1}{3}V,\frac{1}{3}V,\frac{1}{3}V)$. Using this triple any of the original equations gives the same value for λ, namely

$$\lambda=\frac{\partial n}{\partial V_1}\left(\frac{1}{3}V,\frac{1}{3}V,\frac{1}{3}V\right)=\frac{81K^3c_\mathrm{A}V_\mathrm{A}^4}{(3KV_\mathrm{A}+V)^4}.$$

2.4 SEQUENCES, SERIES AND LIMITS

1. Since

$$\lim_{x\to 0}\frac{\Delta T(x)}{x}=-\frac{RT^{*2}}{\Delta H}\lim_{x\to 0}\frac{\ln(1-x)}{x},$$

we must calculate the 0/0 type limit on the right-hand side. By the aid of L'Hospital's rule

$$\lim_{x\to 0}\frac{\ln(1-x)}{x}=\lim_{x\to 0}\frac{-\frac{1}{1-x}}{1}=-1,$$

from which the statement follows directly. Further considerations on the application of L'Hospital's rule can be found in [91].

2. The sequence

$$\left\{\left(1+\frac{V}{KV_1}\frac{1}{i}\right)^i\right\}$$

is of a well-known type so we can state immediately that it is strictly monotonously increasing, bounded and

$$\lim_{i\to\infty}\left(1+\frac{V}{KV_1}\frac{1}{i}\right)^i=e^{\frac{V}{KV_1}}.$$

Thus, the sequence $\{n_i\}$ is strictly monotonously increasing, bounded and

$$S=\lim_{i\to\infty}n_i=c_1^0V_1\left(1-e^{-\frac{V}{KV_1}}\right). \tag{2.59}$$

The strictly monotonously increasing property of $\{n_i\}$ means that the extracted amount of the solute – for a given volume V of the extracting solvent – cannot exceed the limit given by Eqn (2.59) provided the extracting solvent is applied in equal instalments. If we consider S as the function of V then

$$\lim_{V\to\infty}S(V)=c_1^0V_1,$$

that is, for the full extraction of the solute an infinite volume of the extracting solvent would be needed.

3. We first remark that Descartes' rule of signs guarantees the existence of exactly one positive root for both of Eqns (1.39) and (1.40). Thus, we can really consider the unique positive root as a function of the parameter c. For the sake of simplicity let

$$x=\frac{c}{c^{\ominus}}>0,$$

$$h(x)=\frac{[\mathrm{H}^+](c^{\ominus}x)}{c^{\ominus}}>0$$

and

$$h_2(x) = \frac{[\mathrm{H}^+]_2(c^\ominus x)}{c^\ominus} > 0.$$

With these substitutions we obtain the following equations for $h(x)$ and $h_2(x)$:

$$h^3(x) + K_\mathrm{a}h^2(x) - (K_\mathrm{a}x + K_\mathrm{w})h(x) - K_\mathrm{a}K_\mathrm{w} = 0 \tag{2.60}$$

and

$$h_2^2(x) + K_\mathrm{a}h_2(x) - K_\mathrm{a}x = 0. \tag{2.61}$$

Then a rearrangement of Eqn (2.60) yields

$$h^2(x) + K_\mathrm{a}h(x) = K_\mathrm{a}x + K_\mathrm{w} + \frac{K_\mathrm{a}K_\mathrm{w}}{h(x)} \geq K_\mathrm{a}x, \tag{2.62}$$

which implies

$$\frac{h(x)}{x}\,[h(x) + K_\mathrm{a}] \geq K_\mathrm{a}.$$

Thus, $h(x)/x$ has a positive lower bound, that is,

$$\frac{h(x)}{x} \geq A, \tag{2.63}$$

for some $A > 0$. If we substract the equation

$$h_2^2(x) + K_\mathrm{a}h_2(x) = K_\mathrm{a}x$$

obtained by the rearrangement of Eqn (2.61) from Eqn (2.62), we find that

$$[h(x) - h_2(x)]g(x) = \frac{K_aK_\mathrm{w}}{xh(x)} + \frac{K_\mathrm{w}}{x}, \tag{2.64}$$

where

$$g(x) = \frac{h(x) + h_2(x) + K_\mathrm{a}}{x} \geq \frac{h(x)}{x} \geq A.$$

It is easy to see that

$$[h(x) - h_2(x)]\frac{g(x)}{A} \geq [h(x) - h_2(x)] \geq 0. \tag{2.65}$$

According to Eqn (2.63)

$$\frac{K_\mathrm{a}K_\mathrm{w}}{xh(x)} \le \frac{K_\mathrm{a}K_\mathrm{w}}{Ax^2},$$

hence

$$\lim_{x\to\infty}\left(\frac{K_\mathrm{a}K_\mathrm{w}}{xh(x)} + \frac{K_\mathrm{w}}{x}\right) = 0$$

and

$$\lim_{x\to\infty}\left[h(x) - h_2(x)\right]g(x) = 0.$$

Thus, Eqn (2.65) implies

$$\lim_{x\to\infty}\left[h(x) - h_2(x)\right] = 0,$$

which proves the assertion of the problem.

4. Let

$$P_n(x) = \sum_{i=1}^{n} a_i x^i$$

and

$$Q_n(x) = 1 + \sum_{i=1}^{n} b_i x^i$$

be two polynomials of the same degree, and assume that the coefficients in Q_n are positive. In this case

$$\frac{P_n(x)}{Q_n(x)} = \frac{\sum_{i=1}^{n} a_i x^i}{1 + \sum_{i=1}^{n} b_i x^i} = \frac{\sum_{i=1}^{n} \frac{a_i}{x^{n-i}}}{\frac{1}{x^n} + \sum_{i=1}^{n} \frac{b_i}{x^{n-i}}},$$

is valid for $0 < x < \infty$, so

$$\lim_{x\to 0}\frac{P_n(x)}{Q_n(x)} = 0,$$

and

$$\lim_{x\to\infty}\frac{P_n(x)}{Q_n(x)} = \frac{a_n}{b_n}.$$

We apply these results to the terms of sums on the right-hand side of Eqn (1.41):

$$\begin{aligned}\lim_{x\to 0}\frac{k_{2\nu}}{x}\frac{q'_\nu\left(\frac{1}{x}\right)}{q_\nu\left(\frac{1}{x}\right)} &= \lim_{\frac{1}{x}\to\infty}\frac{k_{2\nu}}{x}\frac{q'_\nu\left(\frac{1}{x}\right)}{q_\nu\left(\frac{1}{x}\right)}\\ &= \lim_{\frac{1}{x}\to\infty} k_{2\nu}\frac{\sum_{i=1}^{m} i\left[\prod_{j=1}^{i} k_{Aj}^{(\nu)}\right]\left(\frac{1}{x}\right)^i}{1+\sum_{i=1}^{m}\left[\prod_{j=1}^{i} k_{Aj}^{(\nu)}\right]\left(\frac{1}{x}\right)^i} = k_{2\nu}m\end{aligned}$$

and

$$\lim_{x\to 0} k_{3\nu}x\frac{p'_\nu(x)}{p_\nu(x)} = \lim_{x\to 0} k_{3\nu}\frac{\sum_{i=1}^{l} i\left[\prod_{j=1}^{i}\frac{1}{k_{Bj}^{(\nu)}}\right]x^i}{1+\sum_{i=1}^{l}\left[\prod_{j=1}^{i}\frac{1}{k_{Bj}^{(\nu)}}\right]x^i} = 0.$$

Since all the terms of the sums on the right-hand side of Eqn (1.41) tend to finite limits, the same is valid for the sums themselves. At the same time

$$\lim_{x\to 0}\frac{k_1}{x} = \infty,$$

so the right-hand side of Eqn (1.41) tends to infinity as $x \to 0$. By similar considerations it can be seen that

$$\lim_{x\to\infty}\frac{k_{2\nu}}{x}\frac{q'_\nu(1/x)}{q_\nu(1/x)} = \lim_{(1/x)\to 0}\frac{k_{2\nu}}{x}\frac{q'_\nu(1/x)}{q_\nu(1/x)} = 0$$

and

$$\lim_{x\to\infty} k_{3\nu}x\frac{p'_\nu(x)}{p_\nu(x)} = k_{3\nu}l,$$

so the sums on the right-hand side of Eqn (1.41) tend to finite limits for $x \to \infty$, too. Since

$$\lim_{x\to\infty}\frac{k_1}{x} = 0,$$

the full right-hand side of Eqn (1.41) tends to a finite limit as $x \to \infty$. Now let

$$F(x) = x - G(x),$$

where $G(x)$ denotes the right-hand side of Eqn (1.41). A root of Eqn (1.41) evidently satisfies $F(x)=0$ as well, and conversely. In the light of the previous discussion

$$\lim_{x\to 0} F(x) = -\infty$$

and

$$\lim_{x\to \infty} F(x) = \infty,$$

from which it follows that $F(a)<0$ and $F(b)>0$ for some $b>a>0$. Since F is continuous on $[a,b]$, it takes all the values between $F(a)$ and $F(b)$ on $[a,b]$, and therefore it has a zero in the interval (a,b). Thus, Eqn (1.41) has a positive root.

5. (a) The series in the denominator,

$$\sum_{i=1}^{\infty} x^i = x + x^2 + x^3 + \cdots ,$$

can be written as

$$\sum_{i=1}^{\infty} x^i = \sum_{i=0}^{\infty} x^i - 1 = \frac{1}{1-x} - 1 = \frac{x}{1-x}$$

if $0<x<1$. This series can also be differentiated for $0<x<1$ [30, p. 683], that is,

$$\sum_{i=1}^{\infty} i x^{i-1} = \frac{1}{(1-x)^2}.$$

Multiplying by x

$$\sum_{i=1}^{\infty} i x^{i} = \frac{x}{(1-x)^2},$$

so

$$\frac{n^\sigma(x)}{n^\sigma_{\mathrm{m}}} = \frac{c\frac{x}{(1-x)^2}}{1+c\frac{x}{1-x}} = \frac{cx}{(1-x)[(c-1)x+1]}. \tag{2.66}$$

(b) Using Eqn (2.66)

$$\lim_{x\to 1} \frac{n^\sigma(x)}{n^\sigma_{\mathrm{m}}} = \infty.$$

6. According to a well-known property of Fourier series,

$$B_0 = \frac{1}{L}\int_0^L \phi(\xi)\,\mathrm{d}\xi$$

and

$$B_n = \frac{2}{L}\int_0^L \phi(\xi)\cos\frac{n\pi\xi}{L}\mathrm{d}\xi; \qquad n = 1, 2, 3, \ldots,$$

where

$$\phi(\xi) = \begin{cases} c_0 & \text{if} \quad 0 \le \xi \le L_0, \\ 0 & \text{if} \quad L_0 < \xi \le L. \end{cases}$$

After completing the integrations indicated above we obtain

$$B_0 = \frac{1}{L}\left[\int_0^{L_0} c_0\,\mathrm{d}\xi + \int_{L_0}^{L} 0\,\mathrm{d}\xi\right] = \frac{c_0 L_0}{L}$$

and, for $n = 1, 2, 3, \ldots,$

$$B_n = \frac{2}{L}\left[\int_0^{L_0} c_0\cos\frac{n\pi\xi}{L}\mathrm{d}\xi + \int_{L_0}^{L} 0\cos\frac{n\pi\xi}{L}\mathrm{d}\xi\right] = \frac{2c_0}{n\pi}\sin\frac{n\pi L_0}{L}.$$

If the limit can be taken by terms, it is easy to see that

$$\lim_{t\to\infty} c(x,t) = B_0 = \frac{c_0 L_0}{L}$$

for a fixed x, that is, the diffusing solute will finally be distributed uniformly in the system.

7. For a fixed $x \neq 0$ let

$$\phi(t) = \ln\left[\frac{\sqrt{4\pi D}}{c_0}c(x,t)\right] = -\frac{x^2}{4Dt} - \ln\sqrt{t}, \tag{2.67}$$

that is,

$$\phi(t) = -\frac{x^2 + 4Dt\ln\sqrt{t}}{4Dt}.$$

We shall use transformation

$$t\ln\sqrt{t} = \frac{\ln\sqrt{t}}{1/t}.$$

According to L'Hospital's rule (applied to a 0/0 type limit)

$$\lim_{t\to 0}\frac{-\ln\sqrt{t}}{1/t}=\lim_{t\to 0}\frac{-(1/\sqrt{t})(1/2\sqrt{t})}{-(1/t^2)}$$
$$=\lim_{t\to 0}\left(\frac{t}{2}\right)=0,$$

so

$$\lim_{t\to 0}\frac{\ln\sqrt{t}}{1/t}=-\lim_{t\to 0}\frac{-\ln\sqrt{t}}{1/t}=0,$$

and, for $x\neq 0$,

$$\lim_{t\to 0}\phi(t)=-\infty.$$

But on the basis of Eqn (2.67)

$$c(x,t)=\frac{c_0}{\sqrt{4\pi D}}e^{\phi(t)},$$

and, because of the continuity of the right-hand side,

$$\lim_{t\to 0}c(x,t)=\frac{c_0}{\sqrt{4\pi D}}e^{\lim_{t\to 0}\phi(t)}=0.$$

8. Let

$$\phi(t)=\ln\frac{[\mathrm{B}]_0^2}{4\pi D\,[\mathrm{B}]_\mathrm{r}^2\,t}+4\,[\mathrm{A}]_0\,kt-1,$$

that is,

$$\phi(t)=t\left\{\frac{1}{t}\ln\frac{[\mathrm{B}]_0^2}{4\pi D\,[\mathrm{B}]_\mathrm{r}^2\,t}+4\,[\mathrm{A}]_0\,k-\frac{1}{t}\right\}.$$

By the aid of L'Hospital's rule (the needed limit is of type ∞/∞) we find that

$$\lim_{t\to\infty}\frac{-\ln\frac{[\mathrm{B}]_0^2}{4\pi D[\mathrm{B}]_\mathrm{r}^2 t}}{t}=\lim_{t\to\infty}\frac{1/t}{1}=0,\tag{2.68}$$

so, taking into account

$$\lim_{t\to\infty}\frac{\ln\frac{[\mathrm{B}]_0^2}{4\pi D[\mathrm{B}]_\mathrm{r}^2 t}}{t}=-\lim_{t\to\infty}\frac{-\ln\frac{[\mathrm{B}]_0^2}{4\pi D[\mathrm{B}]_\mathrm{r}^2 t}}{t},$$

we obtain

$$\lim_{t\to\infty} \phi(t) = \infty.$$

Now let

$$\psi(t) = \sqrt{t \ln \frac{[\mathrm{B}]_0^2}{4\pi D\,[\mathrm{B}]_\mathrm{r}^2\, t} + 2\,[\mathrm{A}]_0\, kt^2},$$

that is,

$$\psi(t) = \sqrt{t^2 \left\{ \frac{1}{t} \ln \frac{[\mathrm{B}]_0^2}{4\pi D\,[\mathrm{B}]_\mathrm{r}^2\, t} + 2k\,[\mathrm{A}]_0 \right\}}.$$

From this and Eqn (2.68) we find that

$$\lim_{t\to\infty} \psi(t) = \infty.$$

We shall also need the followings:

$$\begin{aligned} \phi'(t) &= -\frac{1}{t} + 4k\,[\mathrm{A}]_0\,, \\ \lim_{t\to\infty} \phi'(t) &= 4k\,[\mathrm{A}]_0\,, \\ \psi'(t) &= \frac{\frac{1}{t}\ln\frac{[\mathrm{B}]_0^2}{4\pi D[\mathrm{B}]_\mathrm{r}^2 t} - \frac{1}{t} + 4k\,[\mathrm{A}]_0}{2\sqrt{\frac{1}{t}\ln\frac{[\mathrm{B}]_0^2}{4\pi D[\mathrm{B}]_\mathrm{r}^2 t} + 2\,[\mathrm{A}]_0\, k}} \end{aligned}$$

and

$$\lim_{t\to\infty} \psi'(t) = \sqrt{2k\,[\mathrm{A}]_0}.$$

Applying L'Hospital's rule (the limit to be calculated is of type ∞/∞) we have

$$\begin{aligned} v_\infty = \lim_{t\to\infty} v(t) &= \sqrt{\frac{D}{2}} \lim_{t\to\infty} \frac{\phi(t)}{\psi(t)} \\ &= \sqrt{\frac{D}{2}} \lim_{t\to\infty} \frac{\phi'(t)}{\psi'(t)} = \sqrt{\frac{D}{2}} \frac{4k\,[\mathrm{A}]_0}{\sqrt{2k\,[\mathrm{A}]_0}} = 2\sqrt{kD\,[\mathrm{A}]_0}. \end{aligned}$$

Let the average speed of the sprinter be $10\,\mathrm{m\,s^{-1}}$. With the given numerical data and $v_\infty = 10\,\mathrm{m\,s^{-1}}$ the formula

$$k = \frac{v_\infty^2}{4D\,[\mathrm{A}]_0}$$

yields

$$k = 2.5 \times 10^8\,\mathrm{s^{-1}(mol\,m^{-3})^{-1}}.$$

9. (a)

$$\frac{1}{r(\xi,t)}\frac{\mathrm{d}r}{\mathrm{d}t}(\xi,t) = \frac{\alpha_1(\xi)A_1e^{\alpha_1(\xi)t} + \alpha_2(\xi)A_2e^{\alpha_2(\xi)t}}{A_1e^{\alpha_1(\xi)t} + A_2e^{\alpha_2(\xi)t}},$$

so, for a fixed value of ξ,

$$\begin{aligned}\lim_{t\to\infty}\frac{1}{r(\xi,t)}\frac{\mathrm{d}r}{\mathrm{d}t}(\xi,t) &= \lim_{t\to\infty}\frac{\alpha_1(\xi)A_1 + \alpha_2(\xi)A_2e^{[\alpha_2(\xi)-\alpha_1(\xi)]t}}{A_1 + A_2e^{[\alpha_2(\xi)-\alpha_1(\xi)]t}}\\ &= \alpha_1(\xi),\end{aligned}$$

since $\alpha_2(\xi) - \alpha_1(\xi) < 0$.

(b)

$$\alpha_1(\xi) = \frac{\sqrt{1+4b\omega^2\xi^2}-1}{2\xi},$$

therefore

$$\frac{\alpha_1(\xi)}{S(\xi)} = \frac{\sqrt{1+4b\omega^2\xi^2}-1}{2b\xi^2},$$

where

$$b = \left(1 - \frac{\rho^*}{\rho}\right).$$

Applying L'Hospital's rule (the needed limit is of type 0/0) we find

$$\lim_{\xi\to 0}\frac{\alpha_1(\xi)}{S(\xi)} = \omega^2.$$

10. The limit to be calculated is of type 0/0, and L' Hospital's rule yields (for a fixed $s \neq 0$) that

$$\lim_{r_{ii}\to 0}\frac{\sin sr_{ii}}{sr_{ii}} = \lim_{r_{ii}\to 0}\frac{s\cos sr_{ii}}{s\cdot 1} = 1.$$

11. According to L' Hospital's rule (the limit is of type 0/0) we obtain

$$\lim_{r\to 0}\frac{\sin\alpha r}{r}=\lim_{r\to 0}\frac{\alpha\cos\alpha r}{1}=\alpha.$$

At the same time we obviously have

$$\lim_{r\to 0}\frac{\cos\alpha r}{r}=\infty.$$

Using these limits it is clear that

$$\lim_{r\to 0}\psi(r)=\infty$$

for $B\neq 0$. If, however, $B=0$ then

$$\lim_{r\to 0}\psi(r)=A\lim_{r\to 0}\frac{\sin\alpha r}{r}=A\alpha,$$

which is finite for any A.

12. (a) From the formula

$$Z(\nu,T)=\sum_{i=0}^{\infty}e^{-\frac{ih\nu}{kT}}=1+e^{-\frac{h\nu}{kT}}+e^{-\frac{2h\nu}{kT}}+e^{-\frac{3h\nu}{kT}}+\cdots$$

it is clear that we have an infinite geometric series whose common ratio is

$$q=e^{-\frac{h\nu}{kT}}<1.$$

Thus, the series is convergent and its sum is

$$Z(\nu,T)=\frac{1}{1-q}=\frac{1}{1-e^{-\frac{h\nu}{kT}}}\tag{2.69}$$

(b) With the substitution of Eqn (2.69) we obtain a 0/0 type limit, which can be determined by L'Hospital's rule:

$$\lim_{T\to\infty}\frac{\frac{h\nu}{kT}}{1-e^{-\frac{h\nu}{kT}}}=\lim_{T\to\infty}\frac{-\frac{h\nu}{kT^2}}{-\frac{h\nu}{kT^2}e^{-\frac{h\nu}{kT}}}=1.$$

13. (a) According to the transformation

$$\rho(\lambda, T) = 8\pi hc \frac{1/\lambda^5}{e^{(hc/\lambda kT)} - 1}$$

we must determine a ∞/∞ type limit. Several subsequent applications of L'Hospital's rule give

$$\lim_{\lambda \to 0} \rho(\lambda, T) = 8\pi hc \left(\frac{kT}{hc}\right)^5 \lim_{\lambda \to 0} \frac{120}{e^{(hc/\lambda kT)}} = 0.$$

(b)

$$\frac{\hat{\rho}(\lambda, T)}{\rho(\lambda, T)} = \frac{kT}{hc} \frac{e^{(hc/\lambda kT)} - 1}{1/\lambda},$$

which means that we must determine a 0/0 type limit. From L'Hospital's rule

$$\lim_{\lambda \to \infty} \frac{\hat{\rho}(\lambda, T)}{\rho(\lambda, T)} = \frac{kT}{hc} \lim_{\lambda \to \infty} \frac{-\frac{hc}{kT\lambda^2} e^{(hc/\lambda kT)}}{-(1/\lambda^2)} = 1.$$

14. (a) The starting formula is an indeterminate form of type $\frac{0}{0}$. After the first application of L'Hospital's rule another indeterminate form of type $\frac{0}{0}$ occurs. Applying L'Hospital's rule twice we find

$$\lim_{x \to 0} \frac{x^4 e^x}{(e^x - 1)^2} = \lim_{x \to 0} \frac{4x^3 + x^4}{2(e^x - 1)} = \lim_{x \to 0} \frac{12x^2 + 4x^3}{2e^x} = 0.$$

(b) We write $f(T)$ as

$$f(T) = 3\frac{g(T)}{h^3(T)},$$

where

$$g(T) = \int_0^{h(T)} \frac{x^4 e^x}{(e^x - 1)^2} \mathrm{d}x$$

and

$$h(T) = \frac{\Theta_\mathrm{D}}{T}.$$

With this we have arrived at an indeterminate form of type $\frac{0}{0}$. Using L'Hospital's rule

$$\begin{aligned}\lim_{T\to\infty} f(T) &= 3\lim_{T\to\infty} \frac{h^2(T)e^{h(T)}}{3\left[e^{h(T)}-1\right]^2}\\ &= \lim_{T\to\infty} \frac{\left[h^2(T)+2h(T)\right]}{2\left[e^{h(T)}-1\right]}\\ &= \lim_{T\to\infty} \frac{h(T)+1}{e^{h(T)}} = 1.\end{aligned}$$

The rule was applied several times because of the novel indeterminate forms that occurred during the calculations.

15. (a)

$$f(x) = \ln(1+x);$$

$$f'(x) = \frac{1}{1+x}; \qquad f''(x) = -\frac{1}{(1+x)^2}$$

$$f'''(x) = \frac{2\cdot 1}{(1+x)^3}; \quad f^{(4)}(x) = -\frac{3\cdot 2\cdot 1}{(1+x)^4},$$

$$f^{(i)}(x) = \frac{(-1)^{i+1}(i-1)!}{(1+x)^i}.$$

Using these equations the Taylor series of $f(x)$ around $x=0$ is

$$f(x) = \sum_{i=0}^{\infty} \frac{f^{(i)}(0)}{i!}x^i = \sum_{i=1}^{\infty} \frac{(-1)^{i+1}}{i}x^i.$$

This series gives $f(x)$ for $-1<x\le 1$ [30, p. 684], and yields the demanded result at $x=1$:

$$\ln 2 = \sum_{i=1}^{\infty} \frac{(-1)^{i+1}}{i}.$$

So

$$M = 2\ln 2 = 1.3862\ldots.$$

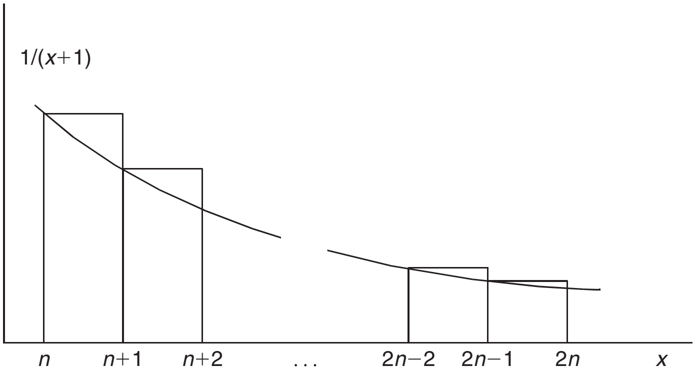


Figure 2.8 A lower estimate of the Madelung constant

(b) i. For small integers the statement can be verified directly. If

$$\sum_{i=1}^{2n} \frac{(-1)^{i+1}}{i} = \sum_{i=n+1}^{2n} \frac{1}{i}$$

then evidently

$$\sum_{i=1}^{2(n+1)} \frac{(-1)^{i+1}}{i} = \left(\sum_{i=n+1}^{2n} \frac{1}{i} \right) + \frac{1}{2n+1} - \frac{1}{2(n+1)}.$$

Adding now the terms $\frac{1}{n+1}$ and $-\frac{1}{2(n+1)}$ on the right-hand side we obtain

$$\sum_{i=1}^{2(n+1)} \frac{(-1)^{i+1}}{i} = \sum_{i=(n+1)+1}^{2(n+1)} \frac{1}{i},$$

which proves the assertion.

ii. On the basis of Figs. 2.8 and 2.9 – taking into account the geometric meaning of a definite integral – it is evident that

$$\int_n^{2n} \frac{1}{x+1} \mathrm{d}x \le a_{2n} \le \int_n^{2n} \frac{1}{x} \mathrm{d}x,$$

that is,

$$\ln \frac{2n+1}{n+1} \le a_{2n} \le \ln 2.$$

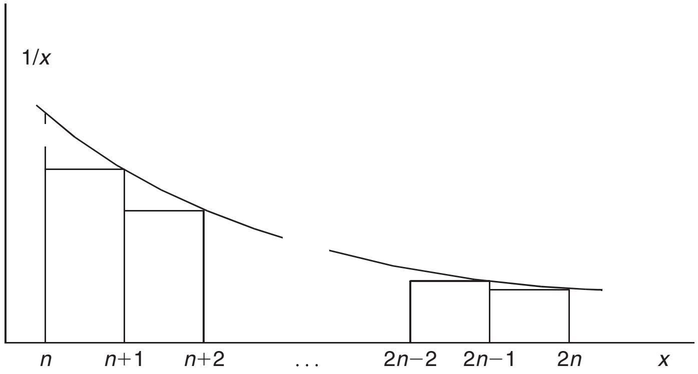


Figure 2.9 An upper estimate of the Madelung constant

Since

$$\lim_{n\to\infty} \ln\frac{2n+1}{n+1} = \ln 2,$$

we have proved that

$$\lim_{n\to\infty} \ln a_{2n} = \ln 2,$$

which means that the sum of the infinite series is also ln 2.

16. We work on the basis of the work [55]. In the case of the first partial sum

$$|i|, |j|, |k| \leq 1,$$

and so

$$i^2 + j^2 + k^2 \leq 3.$$

It is not diffficult to see that any lattice point on a side of the cube has a coordinate whose absolute value is 1. Similarly, any lattice point on an edge of the cube has two coordinates whose absolute values are 1. Finally, the absolute values of the coordinates of a lattice point at a vertex of the cube are $(1, 1, 1)$. Table 2.4 contains the lattice points to be taken into account. In the second column of the table we see the absolute values of the coordinates. The number of the lattice points corresponding to a given triple of the absolute values can be calculated from the formula

$$n = \frac{3!}{(3-n_{\mathrm{a}})!}2^{n_{\mathrm{b}}},$$

Table 2.4 Lattice points in the cube of edge length 2

$i^2+j^2+k^2$	$\|i\|,\|j\|,\|k\|$	Number of lattice points	Multiplier
1	100	6	$\frac{1}{2}$
2	110	12	$\frac{1}{4}$
3	111	8	$\frac{1}{8}$

Table 2.5 Lattice points in the cube of edge length 4

$i^2+j^2+k^2$	$\|i\|,\|j\|,\|k\|$	Number of lattice points	Multiplier
1	100	6	
2	110	12	
3	111	8	
4	200	6	$\frac{1}{2}$
5	210	24	$\frac{1}{2}$
6	211	24	$\frac{1}{2}$
8	220	12	$\frac{1}{4}$
9	221	24	$\frac{1}{4}$
12	222	8	$\frac{1}{8}$

where n_a is the number of the unique elements among the three absolute values of the coordinates and n_b the number of the non-zero elements of the same triple. Using the table

$$\begin{aligned} A_1 &= -\frac{1}{2} \times 6 \times \frac{1}{\sqrt{1}} + \frac{1}{4} \times 12 \times \frac{1}{\sqrt{2}} - \frac{1}{8} \times 8 \times \frac{1}{\sqrt{3}} \\ &= -1.4560\ldots. \end{aligned}$$

In the case of the second partial sum we can think in a similar fashion, the necessary information is included in Table 2.5. In the interpretation of the table notice that the numbers 7, 10 and 11 cannot be given as sums of the

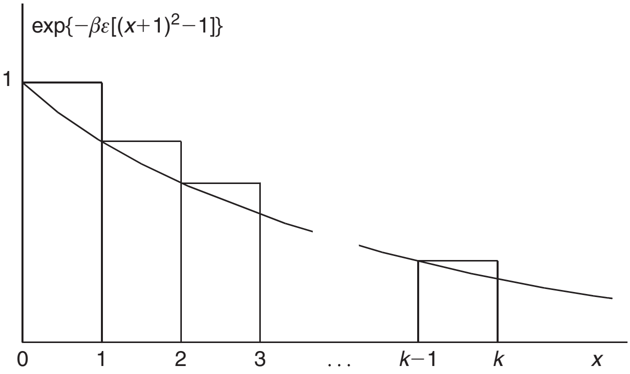


Figure 2.10 A lower estimate of the partial sum $Q_k(\beta\varepsilon)$

squares of three integers (including 0 as well). On the basis of the table the second partial sum is

$$\begin{aligned}A_2 = &-6\times\frac{1}{\sqrt{1}}+12\times\frac{1}{\sqrt{2}}-8\times\frac{1}{\sqrt{3}}\\ &+\frac{1}{2}\left(6\times\frac{1}{\sqrt{4}}-24\times\frac{1}{\sqrt{5}}+24\times\frac{1}{\sqrt{6}}\right)\\ &+\frac{1}{4}\left(12\times\frac{1}{\sqrt{8}}-24\times\frac{1}{\sqrt{9}}\right)+\frac{1}{8}\times 8\times\frac{1}{\sqrt{12}},\end{aligned}$$

that is,

$$A_2 = -1.7517\ldots.$$

The partial sum A_2 is already fairly close to the value of $-M$.

17. (a) Let

$$q_n(\beta\varepsilon) = e^{-(n^2-1)\beta\varepsilon}.$$

Since

$$\frac{q_{n+1}(\beta\varepsilon)}{q_n(\beta\varepsilon)} = e^{-(2n+1)\beta\varepsilon} \le e^{-\beta\varepsilon} < 1$$

for $n = 1, 2, \ldots,$ the ratio test shows that the series is convergent.

(b) Let $Q_k(\beta\varepsilon)$ the kth partial sum of the series investigated. Inspecting Figs. 2.10 and 2.11 and considering the geometrical meaning of a definite integral we can write that

$$\int_0^k e^{-\beta\varepsilon[(x+1)^2-1]}\,\mathrm{d}x \le Q_k(\beta\varepsilon) \le \int_0^k e^{-\beta\varepsilon(x^2-1)}\,\mathrm{d}x.$$

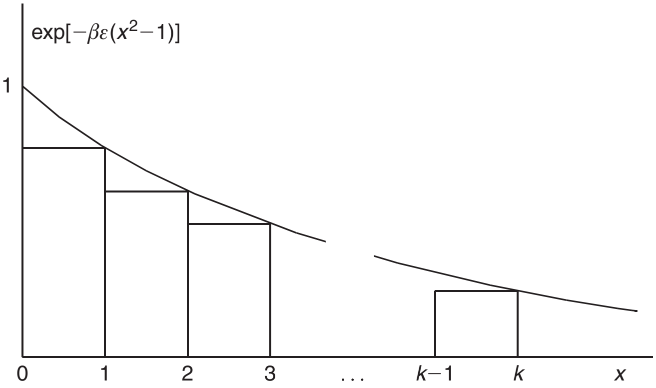


Figure 2.11 An upper estimate of the partial sum $Q_k(\beta\varepsilon)$

The expressions

$$\int_0^k e^{-\beta\varepsilon\left[(x+1)^2-1\right]}\,\mathrm{d}x = e^{\beta\varepsilon}\int_0^k e^{-\beta\varepsilon(x+1)^2}\,\mathrm{d}x,$$

$$\int_0^k e^{-\beta\varepsilon(x+1)^2}\,\mathrm{d}x = \int_1^{k+1} e^{-\beta\varepsilon y^2}\,\mathrm{d}y$$

and

$$\begin{aligned}\int_1^{k+1} e^{-\beta\varepsilon y^2}\,\mathrm{d}y &= -\int_0^1 e^{-\beta\varepsilon y^2}\,\mathrm{d}y + \int_0^k e^{-\beta\varepsilon y^2}\,\mathrm{d}y \\ &\quad + \int_k^{k+1} e^{-\beta\varepsilon y^2}\,\mathrm{d}y,\end{aligned}$$

moreover, the mean-value theorem of the integral calculus implies that

$$\begin{aligned}\int_0^k e^{-\beta\varepsilon\left[(x+1)^2-1\right]}\,\mathrm{d}x &= e^{\beta\varepsilon}\int_1^{k+1} e^{-\beta\varepsilon y^2}\,\mathrm{d}y \\ &\geq e^{\beta\varepsilon}\left[-1 + \int_0^k e^{-\beta\varepsilon y^2}\mathrm{d}y\right. \\ &\qquad \left. + e^{-\beta\varepsilon(k+1)^2}\right].\end{aligned}$$

Since

$$\int_0^k e^{-\beta\varepsilon(x^2-1)}\,\mathrm{d}x = e^{\beta\varepsilon}\int_0^k e^{-\beta\varepsilon x^2}\,\mathrm{d}x$$

is also valid we can write that

$$e^{\beta\varepsilon}\left[\int_0^k e^{-\beta\varepsilon y^2}\,\mathrm{d}y + e^{-\beta\varepsilon(k+1)^2} - 1\right] \le Q_k(\beta\varepsilon) \le e^{\beta\varepsilon}\int_0^k e^{-\beta\varepsilon x^2}\,\mathrm{d}x.$$

Thus, for the limit $q(\beta\varepsilon)$ of the sequence $Q_k(\beta\varepsilon)$

$$e^{\beta\varepsilon}\left(\frac{1}{2}\sqrt{\frac{\pi}{\beta\varepsilon}} - 1\right) \le q(\beta\varepsilon) \le \frac{1}{2}e^{\beta\varepsilon}\sqrt{\frac{\pi}{\beta\varepsilon}},$$

that is,

$$e^{\beta\varepsilon}\left(1 - 2\sqrt{\frac{\beta\varepsilon}{\pi}}\right) \le 2q(\beta\varepsilon)\sqrt{\frac{\beta\varepsilon}{\pi}} \le e^{\beta\varepsilon}$$

holds. From this latter relationship it follows that

$$2q(\beta\varepsilon)\sqrt{\frac{\beta\varepsilon}{\pi}} \to 1$$

for $\beta\varepsilon \to 0$.

2.5 DIFFERENTIAL EQUATIONS

1. (a) Suppose that [A] does not become zero. A rearrangement of the differential equation yields

$$\int_0^t \frac{1}{[\mathrm{A}](\tau)}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}\tau}(\tau)\,\mathrm{d}\tau = -k\int_0^t 1\,\mathrm{d}\tau,$$

and after integration we obtain

$$\ln\frac{[\mathrm{A}](t)}{[\mathrm{A}]_0} = -kt,$$

that is,

$$[\mathrm{A}](t) = [\mathrm{A}]_0 e^{-kt}. \tag{2.70}$$

(b) On the basis of paragraph 1a

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}(t) = k[\mathrm{A}]_0 e^{-kt}; \qquad [\mathrm{P}](0) = [\mathrm{P}]_0,$$

which can be integrated directly:

$$[\mathrm{P}](t) = [\mathrm{P}]_0 + [\mathrm{A}]_0\left(1 - e^{-kt}\right).$$

(c) Adding the differential equations in the problem we find

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} + \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = 0,$$

which means that

$$\frac{\mathrm{d}}{\mathrm{d}t}\left([\mathrm{A}] + [\mathrm{P}]\right) = 0.$$

Thus, $[\mathrm{A}] + [\mathrm{P}]$ is a constant function, and, because of the initial conditions,

$$[\mathrm{A}] + [\mathrm{P}] = [\mathrm{A}]_0 + [\mathrm{P}]_0.$$

(d) On the basis of the Eqn (2.70)

$$\frac{[\mathrm{A}]_0}{2} = [\mathrm{A}](t_{1/2}) = [\mathrm{A}]_0 e^{-kt_{1/2}},$$

from which

$$t_{1/2} = \frac{\ln 2}{k}.$$

2. (a) Assume that the function [A] never becomes zero. Rearranging and integrating the differential equation we obtain

$$\int_0^t \frac{1}{[\mathrm{A}]^n(\tau)} \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}\tau}(\tau)\,\mathrm{d}\tau = -k\int_0^t 1\,\mathrm{d}\tau,$$

that is,

$$\frac{1}{(1-n)}[\mathrm{A}]^{1-n}(t) = \frac{1}{(1-n)}[\mathrm{A}]_0^{1-n} - kt. \tag{2.71}$$

(b) By the aid of Eqn (2.71)

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}(t) = k[\mathrm{A}]^n(t) = k\left\{[\mathrm{A}]_0^{1-n} - (1-n)kt\right\}^{\frac{n}{1-n}};\ [\mathrm{P}](0) = [\mathrm{P}]_0,$$

and integrating this we arrive at

$$[\mathrm{P}](t) = [\mathrm{A}]_0 + [\mathrm{P}]_0 - \frac{1}{\left\{[\mathrm{A}]_0^{-(n-1)} + (n-1)kt\right\}^{\frac{1}{n-1}}}.$$

(c) See paragraph 1c.

(d) Using Eqn (2.71)

$$kt_{1/2} = \frac{[\mathrm{A}]_0^{1-n}}{(1-n)} - \frac{\left(\frac{[\mathrm{A}]_0}{2}\right)^{1-n}}{(1-n)},$$

so

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k[\mathrm{A}]_0^{n-1}}.$$

3. The initial value problem to be solved is

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}(t) = k[\mathrm{A}]_0 e^{-kt} - k'[\mathrm{B}](t); \qquad [\mathrm{B}](0) = [\mathrm{B}]_0. \tag{2.72}$$

Since

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}(t) + k'[\mathrm{B}](t) = e^{-k't}\frac{\mathrm{d}}{\mathrm{d}t}\left\{e^{k't}[\mathrm{B}](t)\right\},$$

Eqn (2.72) can be rewritten as

$$e^{-k't}\frac{\mathrm{d}}{\mathrm{d}t}\left\{e^{k't}[\mathrm{B}](t)\right\} = k[\mathrm{A}]_0 e^{-kt}. \tag{2.73}$$

If $k = k'$ then

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\{e^{kt}[\mathrm{B}](t)\right\} = k[\mathrm{A}]_0,$$

and an integration followed by a rearrangement yields

$$[\mathrm{B}](t) = \{k[\mathrm{A}]_0 t + [\mathrm{B}]_0\}e^{-kt}.$$

If, however, $k \neq k'$ then a rearrangement of Eqn (2.73) gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\{e^{k't}[\mathrm{B}](t)\right\} = k[\mathrm{A}]_0 e^{(k'-k)t},$$

and after integration

$$[\mathrm{B}](t) = \frac{k[\mathrm{A}]_0}{k'-k}\left(e^{-kt} - e^{-k't}\right) + [\mathrm{B}]_0 e^{-k't}.$$

4. (a) Subtracting the two differential equations from each other we find

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} - \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = 0,$$

which implies

$$\frac{\mathrm{d}}{\mathrm{d}t}\{[\mathrm{A}] - [\mathrm{B}]\} = 0.$$

According to this equation $[\mathrm{A}] - [\mathrm{B}]$ is a time-independent constant function. Because of the initial conditions

$$[\mathrm{A}] - [\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{B}]_0,$$

and if we express [B] from this and insert into the differential equation for [A] we obtain the differential equation

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k[\mathrm{A}]\{[\mathrm{B}]_0 - [\mathrm{A}]_0 + [\mathrm{A}]\}, \tag{2.74}$$

which already contains only one unknown function.

(b) Assume that the functions [A] and [B] never become zero. Rearranging and integrating Eqn (2.74) we obtain

$$\int_0^t \frac{1}{[\mathrm{A}](\tau)\{[\mathrm{B}]_0 - [\mathrm{A}]_0 + [\mathrm{A}](\tau)\}}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}\tau}(\tau)\mathrm{d}\tau = -k\int_0^t 1\,\mathrm{d}\tau,$$

that is,

$$\frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\ln\frac{[\mathrm{A}]_0\,\{[\mathrm{B}]_0 - [\mathrm{A}]_0 + [\mathrm{A}](t)\}}{[\mathrm{B}]_0[\mathrm{A}](t)} = kt.$$

5. (a) By adding the two differential equations it can be seen that

$$\frac{\mathrm{d}}{\mathrm{d}t}\{[\mathrm{A}]+[\mathrm{B}]\}=\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}+\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=0.$$

So $[\mathrm{A}]+[\mathrm{B}]$ is a constant function, and, because of the initial conditions,

$$[\mathrm{A}]+[\mathrm{B}]=[\mathrm{A}]_0+[\mathrm{B}]_0. \tag{2.75}$$

Solve now this equation for [A] and insert the formula obtained into the differential equation for [B]. In this way we find the differential equation

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=k[\mathrm{B}]^2\{[\mathrm{A}]_0+[\mathrm{B}]_0-[\mathrm{B}]\} \tag{2.76}$$

we have searched for.

(b) Assume that the functions [A] and [B] never become zero. Rearranging and integrating Eqn (2.76) we find

$$\int_0^t \frac{1}{[\mathrm{B}]^2(\tau)\{[\mathrm{A}]_0+[\mathrm{B}]_0-[\mathrm{B}](\tau)\}}\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}\tau}(\tau)\,\mathrm{d}\tau=k\int_0^t 1\,\mathrm{d}\tau$$

and

$$\frac{[\mathrm{B}](t)-[\mathrm{B}]_0}{[\mathrm{B}](t)[\mathrm{B}]_0\left([\mathrm{A}]_0+[\mathrm{B}]_0\right)}-\frac{\ln\frac{[\mathrm{B}]_0\{[\mathrm{A}]_0+[\mathrm{B}]_0-[\mathrm{B}](t)\}}{[\mathrm{A}]_0[\mathrm{B}](t)}}{\{[\mathrm{A}]_0+[\mathrm{B}]_0\}^2}=kt.$$

Unfortunately, it is impossible to explicitly express $[\mathrm{B}](t)$ from this equation. Nevertheless, the equation unambiguously defines the function [B] in an implicate form.

6. (a) See paragraph 5a. In this case the separate differential equation needed is

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=-(k+k')[\mathrm{A}]+k'\{[\mathrm{A}]_0+[\mathrm{B}]_0\}.$$

(b) Suppose that the function $(\mathrm{d}[\mathrm{A}]/\mathrm{d}t)$ never becomes zero. Rearranging and integrating the previous differential equation we obtain

$$\int_0^t \frac{1}{k'\{[\mathrm{A}]_0+[\mathrm{B}]_0\}-(k+k')[\mathrm{A}](\tau)}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}\tau}(\tau)\,\mathrm{d}\tau=\int_0^t 1\,\mathrm{d}\tau,$$

and then

$$-\frac{1}{k+k'}\ln\frac{k'\{[\mathrm{A}]_0+[\mathrm{B}]_0\}-(k+k')[\mathrm{A}](\tau)}{k'\{[\mathrm{A}]_0+[\mathrm{B}]_0\}-(k+k')[\mathrm{A}]_0}=t,$$

from which it follows that

$$[\mathrm{A}](t)=\frac{k'\{[\mathrm{A}]_0+[\mathrm{B}]_0\}+\{k[\mathrm{A}]_0-k'[\mathrm{B}]_0\}e^{-(k+k')t}}{k+k'}.$$

Utilizing the latter formula

$$\begin{aligned}[\mathrm{B}](t)&=[\mathrm{A}]_0+[\mathrm{B}]_0-[\mathrm{A}](t)\\&=\frac{k\{[\mathrm{A}]_0+[\mathrm{B}]_0\}+\{k'[\mathrm{B}]_0-k[\mathrm{A}]_0\}e^{-(k+k')t}}{k+k'}.\end{aligned}$$

(c)

$$\lim_{t\to\infty}\frac{[\mathrm{B}](t)}{[\mathrm{A}](t)}=\frac{k}{k'},$$

the formula expresses the establishment of the equilibrium state.

7. A rearrangement of the original differential equation yields

$$e^{-\int_0^t f(\tau)\mathrm{d}\tau}\frac{\mathrm{d}}{\mathrm{d}t}\left(x(t)e^{\int_0^t f(\tau)\mathrm{d}\tau}\right)=\dot{x}(t)+f(t)x(t)=g(t),$$

that is,

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(x(t)e^{\int_0^t f(\tau)\mathrm{d}\tau}\right)=g(t)e^{\int_0^t f(\tau)\mathrm{d}\tau},$$

and the integrated form of the latter leads to

$$x(t)=e^{-\int_0^t f(\tau)\mathrm{d}\tau}\left[\int_0^t g(\tau)e^{\int_0^\tau f(\xi)\mathrm{d}\xi}\mathrm{d}\tau+x(0)\right].$$

Because of $g(t)\geq 0$ the integral in the square brackets is non-negative, therefore it is easy to see that $x(t)>0$ if $x(0)>0$.

8. The right-hand side of the differential equation consists of differentiable functions, so the second derivative of b exists, and

$$\frac{\mathrm{d}^2b}{\mathrm{d}t^2}(t)=-k_1^2a_0e^{-k_1t}-4k_2b(t)\frac{\mathrm{d}b}{\mathrm{d}t}(t).\tag{2.77}$$

If b has a local extremum at ξ then $(\mathrm{d}b/\mathrm{d}t)(\xi) = 0$, and Eqn (2.77) yields

$$\frac{\mathrm{d}^2 b}{\mathrm{d}t^2}(\xi) = -k_1^2 a_0 e^{-k_1 \xi} < 0. \tag{2.78}$$

Thus, the sufficient condition of the existence of a local maximum is fulfilled at ξ, which means that any local extremum of b must be a local maximum. So only one local extremum can be attained.

In a more detailed approach suppose that the function $\dot{b}$ has two zeros, one at t_1 and the other at t_2 ($t_1 < t_2$). On the basis of the mean value theorem there is a point ξ in the interval (t_1, t_2) for which $\dot{b}(\xi) = 0$. Since there is a local strict maximum at t_1 an additional application of the mean-value theorem yields that there exists a value $\tau < \xi$ in the interval (t_1, t_2) at which $\dot{b}(\tau) < 0$. Let ξ_m be the highest lower bound (the infimum) of the zeros of $\dot{b}$ that belong to the interval (τ, t_2). Because of the continuity of $\dot{b}$ it follows that $\dot{b}(\xi_\mathrm{m}) = 0$, $\xi_\mathrm{m} > \tau$ and only $\dot{b} < 0$ is possible in the interval (τ, ξ_m). However, Eqn (2.78) requires the existence of a local strict maximum at ξ_m, which means that there exists a point η in the interval (τ, ξ_m) at which $\dot{b}(\eta) > 0$. This is a contradiction, which proves again that the function b can exhibit at most one local extremum.

9. The first equation of the system can be solved separately, and the solution,

$$b_1(t) = b_1(0)e^{-k_1 t},$$

is evidently a strictly monotonous function. For the subscripts $1 < i \leq N - 1$

$$\dot{b}_i(t) = k_{i-1} b_{i-1}(t) - k_i b_i(t),$$

so by differentiation and some rearrangements

$$e^{-k_i t} \frac{\mathrm{d}}{\mathrm{d}t}\left[e^{k_i t} \dot{b}_i(t)\right] = \ddot{b}_i(t) + k_i \dot{b}_i(t) = k_{i-1} \dot{b}_{i-1}(t),$$

that is,

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[e^{k_i t} \dot{b}_i(t)\right] = k_{i-1} \dot{b}_{i-1}(t) e^{k_i t}.$$

Notice now that $e^{k_i t} \neq 0$. If the function $\dot{b}_{i-1}$ has at most $i - 2$ zeros then the same is valid for whole right-hand side and so for the derivative on the left-hand side too. If the first derivative of b_i had more than $i - 1$ zeros, the same would be true for the function defined by the expression in the square brackets, and – according to the mean-value theorem – the derivative of this function would have at least $i-1$ zeros. However, this latter is impossible. Since we have already seen that the curve of the function b_1 does not exhibit any local extremum, the proof is complete for the subscripts $1 < i \leq N-1$. We already know that the right-hand side of the equation

$$\ddot{b}_N(t) = k_{N-1}\dot{b}_{N-1}(t)$$

obtained by differentiation can have at most $N-2$ zeros. So the same is valid for the second derivative of b_N, which – together with the mean-value theorem – implies that at most $N-1$ zeros may occur on the curve of $\dot{b}_N$. This corresponds to at most $N-1$ local extrema, which completes the proof. Notice that for a positive solution – which corresponds to the requirements of chemistry – the derivative of b_1 is negative and that of b_N is positive, which means that b_1 strictly monotonously decreases while b_n strictly monotonously increases in time. It is a further question whether which k_i values and initial conditions will actually ensure the existence of the extrema investigated above.

10. (a) Let

$$g(t) = F(x(t), y(t)).$$

Then

$$\dot{g}(t) = \frac{\partial F}{\partial u}(x(t), y(t))\dot{x}(t) + \frac{\partial F}{\partial v}(x(t), y(t))\dot{y}(t)$$

so

$$\begin{aligned}\dot{g}(t) &= x^{k_3-1}(t)y^{k_1}(t)e^{-k_2[x(t)+y(t)]}[k_3 - k_2x(t)]x(t)[k_1 - k_2y(t)]\\ &\quad + y^{k_1-1}(t)x^{k_3}(t)e^{-k_2[x(t)+y(t)]}[k_1 - k_2y(t)]y(t)[k_2x(t) - k_3]\\ &= 0.\end{aligned}$$

Thus, F really is a first integral of the system investigated.

(b) We show that in the first quadrant $(u, v > 0)$ F is a positive function with one local maximum. From this it is evident that in the first quadrant the curves $F(u, v) = c$ are closed for appropriate $c > 0$ values. The end point p of the interval containing the appropriate values of c will be the maximal value of F. The equations

$$\frac{\partial F}{\partial u}(u_{\mathrm{m}}, v_{\mathrm{m}}) = u_{\mathrm{m}}^{k_3-1}v_{\mathrm{m}}^{k_1}e^{-k_2(u_{\mathrm{m}}+v_{\mathrm{m}})}(k_3 - k_2u_{\mathrm{m}}) = 0,$$

$$\frac{\partial F}{\partial v}(u_{\mathrm{m}}, v_{\mathrm{m}}) = u_{\mathrm{m}}^{k_3}v_{\mathrm{m}}^{k_1-1}e^{-k_2(u_{\mathrm{m}}+v_{\mathrm{m}})}(k_1 - k_2v_{\mathrm{m}}) = 0$$

imply that in the first quadrant a local extremum can only occur at the point

$$u_\mathrm{m} = \frac{k_3}{k_2}; \qquad v_\mathrm{m} = \frac{k_1}{k_2}.$$

The actual occurrence of a local extremum – a maximum – follows from the equations

$$\begin{aligned}
\frac{\partial^2 F}{\partial u^2}(u_\mathrm{m}, v_\mathrm{m}) &= -k_2 u_\mathrm{m}^{k_3-1} v_\mathrm{m}^{k_1} e^{-k_2(u_\mathrm{m}+v_\mathrm{m})} < 0,\\
\frac{\partial^2 F}{\partial v^2}(u_\mathrm{m}, v_\mathrm{m}) &= -k_2 u_\mathrm{m}^{k_3} v_\mathrm{m}^{k_1-1} e^{-k_2(u_\mathrm{m}+v_\mathrm{m})} < 0,\\
\frac{\partial^2 F}{\partial v \partial u}(u_\mathrm{m}, v_\mathrm{m}) &= \frac{\partial^2 F}{\partial xu \partial v}(u_\mathrm{m}, v_\mathrm{m}) = 0,
\end{aligned}$$

which lead to

$$\frac{\partial^2 F}{\partial u^2}(u_\mathrm{m}, v_\mathrm{m}) \frac{\partial^2 F}{\partial v^2}(u_\mathrm{m}, v_\mathrm{m}) - \left[\frac{\partial^2 F}{\partial v \partial u}(u_\mathrm{m}, v_\mathrm{m})\right]^2 > 0.$$

Further calculation shows that

$$p = F(u_\mathrm{m}, v_\mathrm{m}) = \left(\frac{k_3}{k_2}\right)^{k_3} \left(\frac{k_1}{k_2}\right)^{k_1} e^{-(k_1+k_3)} > 0.$$

11. Let $x_0 = (K_4/K_3)$ and $y_0 = (K_1/K_2)$. For the new variables $u = x_0 - x$ and $v = y_0 - y$ we can write that

$$\dot{u} = -K_2 v; \qquad \dot{v} = K_3 u.$$

From this we obtain

$$\ddot{u} = -K_2 K_3 u,$$

which is a well-known differential equation with the general solution

$$u(t) = A_1 \sin \omega t + A_2 \cos \omega t,$$

where A_1 and A_2 are arbitrary constants and $\omega = \sqrt{K_2 K_3}$. Now a simple integration yields

$$v(t) = -\frac{A_1 K_3}{\omega} \cos \omega t + \frac{A_2 K_3}{\omega} \sin \omega t.$$

Thus, the frequency of the periodic solutions is

$$\nu = \frac{1}{2\pi}\sqrt{K_2K_3}.$$

12. (a) For the function g defined by

$$g(t) = F(c_1(t), c_2(t), \dots, c_N(t)) = \sum_{i=1}^{N} M_i c_i(t)$$

we can write that

$$\begin{aligned}\dot{g}(t) &= \sum_{i=1}^{N} M_i \dot{c}_i(t)\\ &= \sum_{i=1}^{N} M_i \left[\sum_{j=1}^{R} \nu_{ij} w_j\left(c_1(t), c_2(t), \dots, c_N(t)\right)\right]\\ &= \sum_{j=1}^{R} w_j\left(c_1(t), c_2(t), \dots, c_N(t)\right)\left(\sum_{i=1}^{N} \nu_{ij} M_i\right) = 0,\end{aligned}$$

which means that F actually is a first integral.

(b) Since

$$\begin{aligned}\sum_{i=1}^{N} M_i \dot{c}_i &= \sum_{i=1}^{N} M_i \left(\sum_{j=1}^{R} \nu_{ij} w_j\right)\\ &= \sum_{j=1}^{R}\left(\sum_{i=1}^{N} \nu_{ij} M_i\right) w_j = 0,\end{aligned}$$

it follows that

$$\sum_{i=1}^{N-1} M_i \dot{c}_i = -M_N \dot{c}_N. \tag{2.79}$$

For simplicity, we renumber the substances so that $\xi = N$ be valid. Now the right-hand side of Eqn (2.79) is of constant sign, so the function $\sum_{i=1}^{N-1} M_i c_i$ is strictly monotonous, that is, aperiodic. This means that at least one of the functions $c_1, c_2, \dots, c_{N-1}$ also is aperiodic.

13. If $(c_1, c_2, \ldots, c_K)$ is a non-constant solution then differentiating the function g defined by

$$g(t) = V(c_1(t), c_2(t), \ldots, c_N(t))$$

we obtain

$$\begin{aligned}\dot{g}(t) &= \sum_{i=1}^{N} \frac{\partial V}{\partial u_i}(c_1(t), c_2(t), \ldots, c_N(t))\dot{c}_i(t)\\ &= \sum_{i=1}^{N} f_i^2(c_1(t), c_2(t), \ldots, c_N(t)) > 0,\end{aligned}$$

which means that g is a strictly monotonously increasing function ($\dot{g}$ may vanish only for the constant solutions $(c_1, c_2, \ldots, c_N)$ since these are the only ones for which all the quantities $f_i(c_1(t), c_2(t), \ldots, c_N(t))$ become zero at the same moment of time). If $(c_1, c_2, \ldots, c_N)$ were a non-constant periodic solution then g would also be periodic, which would lead to a contradiction.

14. (a) Adding the equations of the investigated system we obtain

$$\dot{f}(t) + k_0 f(t) = k_0 \sum_{i=1}^{N} M_i c_{i0}; \qquad f(0) = \sum_{i=1}^{N} M_i c_i^0,$$

from which – according to the theory of first-order differential equations –

$$f(t) = \frac{\int_0^t k_0 \left(\sum_{i=1}^{N} M_i c_{i0}\right) e^{k_0 \tau} \mathrm{d}\tau + f(0)}{e^{k_0 t}}.$$

Since the quantities c_{i0} are not all zeros,

$$\lim_{t\to\infty} \frac{\int_0^t k_0 \left(\sum_{i=1}^{N} M_i c_{i0}\right) e^{k_0 \tau} \mathrm{d}\tau + f(0)}{e^{k_0 t}}$$

is of type ∞/∞, and L' Hospital's rule gives

$$\begin{aligned}&\lim_{t\to\infty} \frac{\int_0^t k_0 \left(\sum_{i=1}^{N} M_i c_{i0}\right) e^{k_0 \tau} \mathrm{d}\tau + f(0)}{e^{k_0 t}}\\ &\qquad = \lim_{t\to\infty} \frac{k_0 \left(\sum_{i=1}^{N} M_i c_{i0}\right) e^{k_0 t}}{k_0 e^{k_0 t}},\end{aligned}$$

that is,

$$\lim_{t\to\infty} f(t) = \sum_{i=1}^{N} M_i c_{i0}. \tag{2.80}$$

(b) Because of Eqn (2.80) each solution is bounded.

(c) If $(c_1, c_2, \dots, c_N)$ is a periodic solution then f is also periodic. So Eqn (2.80) can be valid only if $f(t) = \sum_{i=1}^{N} M_i c_{i0}$ in the full domain of definition of f.

15. We work on the basis of the references [58, 59]. Let us introduce the following notation:

$$\bar{v}_{-j} = k_{-j} \prod_{i=1}^{N} \bar{c}_i^{\nu_{-ij}}$$

and

$$\bar{v}_{+j} = k_{+j} \prod_{i=1}^{N} \bar{c}_i^{\nu_{+ij}},$$

moreover,

$$w_{-j}(c_1, c_2, \dots, c_N) = \frac{v_{-j}(c_1, c_2, \dots, c_N)}{\bar{v}_{-j}} = \prod_{i=1}^{N} \left(\frac{c_i}{\bar{c}_i}\right)^{\nu_{-ij}}$$

and

$$w_{+j}(c_1, c_2, \dots, c_N) = \frac{v_{+j}(c_1, c_2, \dots, c_N)}{\bar{v}_{+j}} = \prod_{i=1}^{N} \left(\frac{c_i}{\bar{c}_i}\right)^{\nu_{+ij}}.$$

With these definitions

$$\begin{aligned} v_{-j} &= \bar{v}_{-j} w_{-j}, \\ v_{+j} &= \bar{v}_{+j} w_{+j} \end{aligned}$$

and

$$v_{-j} - v_{+j} = \bar{v}_{-j} w_{-j} - \bar{v}_{+j} w_{+j}.$$

Because of the principle of detailed balance

$$\bar{v}_{-j} = \bar{v}_{+j},$$

so

$$v_{-j} - v_{+j} = \bar{v}_{-j}(w_{-j} - w_{+j}). \tag{2.81}$$

The first derivative of g is

$$\dot{g} = \sum_{i=1}^{N} \left[\dot{c}_i \ln \frac{c_i}{\bar{c}_i} \right],$$

and, by the aid of Eqns (1.65) and (2.81),

$$\dot{g} = \sum_{j=1}^{R} \bar{v}_{-j}(w_{-j} - w_{+j}) \sum_{i=1}^{N} (v_{+ij} - v_{-ij}) \ln \frac{c_i}{\bar{c}_i}.$$

Using the transformations

$$\sum_{i=1}^{N} (v_{+ij} - v_{-ij}) \ln \frac{c_i}{\bar{c}_i} = \ln \prod_{i=1}^{N} \left(\frac{c_i}{\bar{c}_i} \right)^{v_{+ij} - v_{-ij}}$$

$$\sum_{i=1}^{N} (v_{+ij} - v_{-ij}) \ln \frac{c_i}{\bar{c}_i} = \ln \frac{w_{+j}}{w_{-j}}$$

finally we find that

$$\dot{g} = \sum_{j=1}^{R} \bar{v}_{-j}(w_{-j} - w_{+j}) \ln \frac{w_{+j}}{w_{-j}}.$$

Since $(w_{-j} - w_{+j})$ and $\ln{(w_{+j})}/(w_{-j})$ are of opposite signs, each term of the sum on the right-hand side of $\dot{g}$ is non-positive. Thus, $\dot{g}(t)$ can be zero only at a moment t when all the terms of the sum on the right-hand side are separately zeros. At this moment, however, the right-hand side of Eqn (1.65) vanishes because of Eqn (2.81), so the investigated solution is a constant solution. Thus, for a non-constant solution $\dot{g} < 0$ in the full domain of definition, which means that g strictly monotonously decreases. This, however, is impossible if the investigated solution $(c_1, c_2, \ldots, c_N)$ is periodic, since in this case g should also be periodic.

16. The results are shown in Figs. 2.12 and 2.13. These figures suggest that a closed curve (trajectory) should exist in the xy plane, which corresponds to a periodic solution. The solution that we determined numerically "tends"

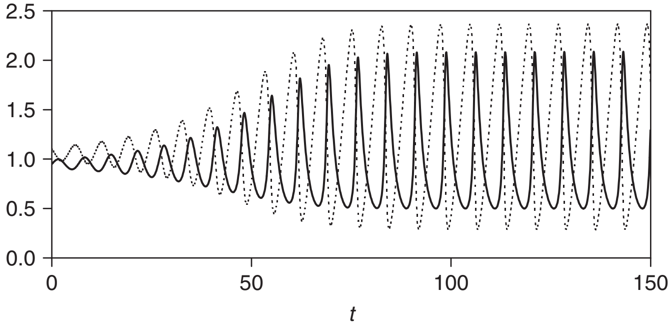


Figure 2.12 The solution of the Autocatalator model; continuous line: x; dashed line: y

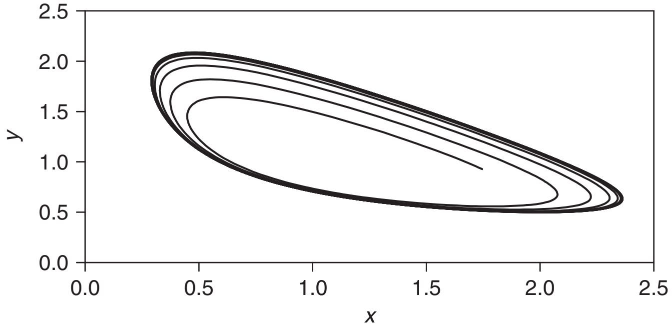


Figure 2.13 The solution of the Autocatalator model in the phase plane xy

to this periodic solution, its curve (trajectory) "spiralizes" towards the curve (trajectory) of the periodic solution. For a detailed treatment of the trajectories of autonomous differential systems see reference [75].

17. (a) Rearranging and integrating the differential equation we obtain

$$\int_0^t r(\tau)\frac{\mathrm{d}r}{\mathrm{d}\tau}(\tau)\,\mathrm{d}\tau = -D\int_0^t 1\,\mathrm{d}\tau,$$

that is,

$$\frac{1}{2}\left[r^2(t) - r_0^2\right] = -Dt,$$

from which

$$r(t) = \sqrt{r_0^2 - 2Dt}.$$

It is evident that this solution is defined only on the finite time interval $[0, (r_0^2/2D))$.

(b) The radius r decreases as time t proceeds, so – as the differential equation shows – the absolute value of the rate of decrease, $|(\mathrm{d}r/\mathrm{d}t)|$, increases. Thus, the initially slow shrinkage of a ring becomes faster and faster in time. In principle the absolute value of the rate of shrinkage becomes infinitely high as $t \to (r_0^2/2D)$.

18. (a) With the substitution $v = \dot{x}$ the problem to be solved can be written as

$$\dot{v} + \frac{k}{m}v = \frac{q}{m}E; \qquad v(0) = v_0,$$

and the standard theory of first-order differential equations (cf. problem 7) yields

$$\begin{aligned} v(t) &= e^{-(k/m)t}\left[\int_0^t \frac{qE}{m}e^{(k/m)\tau}\,\mathrm{d}\tau + v_0\right] \\ &= \frac{qE}{k} + \left(v_0 - \frac{qE}{k}\right)e^{-(k/m)t}. \end{aligned} \tag{2.82}$$

The function x can be obtained by a further integration:

$$\begin{aligned} x(t) &= x_0 + \int_0^t v(\tau)\,\mathrm{d}\tau \\ &= x_0 + \frac{qE}{k}t + \left(\frac{mv_0}{k} - \frac{qEm}{k^2}\right)\left(1 - e^{-(k/m)t}\right). \end{aligned}$$

(b) From Eqn (2.82)

$$v_\infty = \lim_{t\to\infty} \dot{x}(t) = \frac{qE}{k},$$

and for $v_0 = 0$

$$v(t) = v_\infty\left(1 - e^{-(k/m)t}\right).$$

If $v(t) = 0.9v_\infty$ then

$$t = -\frac{m}{k}\ln 0.1 = 9 \times 10^{-14}\,\mathrm{s}.$$

19. Using the notation $p = k/m$ and $q = (1-(\rho^*/\rho))\omega^2$ the problem to be solved is

$$\ddot{r} + p\dot{r} - qr = 0; \qquad r(0) = r_0; \quad \dot{r}(0) = v_0.$$

The general solution of this second-order linear differential equation is

$$r(t) = A_1 e^{\alpha_1 t} + A_2 e^{\alpha_2 t},$$

where A and B are constants to be determined from the initial conditions while α_1 and α_2 are the solutions of the quadratic equation

$$\alpha^2 + p\alpha - q = 0,$$

that is,

$$\alpha_{1,2} = \frac{-p \pm \sqrt{p^2 + 4q}}{2}.$$

Since the quantity under the radical sign is positive, α_1 and α_2 are real, and evidently $\alpha_1 \neq \alpha_2$. On the basis of the initial conditions

$$\begin{aligned} r_0 &= A_1 + A_2 \\ v_0 &= \alpha_1 A_1 + \alpha_2 A_2, \end{aligned}$$

from which

$$A_1 = \frac{v_0 - \alpha_2 r_0}{\alpha_1 - \alpha_2}; \qquad A_2 = -\frac{v_0 - \alpha_1 r_0}{\alpha_1 - \alpha_2}.$$

20. (a) Rearranging and integrating the differential equation we obtain

$$\int_{T_0}^{T} \frac{1}{V(\tau)} \frac{\mathrm{d}V}{\mathrm{d}\tau}(\tau)\, d\tau = \frac{1}{1-\kappa} \int_{T_0}^{T} \frac{1}{\tau} \mathrm{d}\tau,$$

that is,

$$\ln \frac{V(T)}{V_0} = \frac{1}{1-\kappa} \ln \frac{T}{T_0},$$

which leads to the usual formula

$$\frac{V(T)}{V_0} = \left(\frac{T}{T_0}\right)^{(1/1-\kappa)}. \tag{2.83}$$

(b) From Eqn (2.83)

$$V(T) = V_0 \left(\frac{T}{T_0}\right)^{(1/1-\kappa)},$$

so

$$p(T) = nRTV^{-1}(T) = nRV_0^{-1}T_0^{-1/(\kappa-1)}T^{\kappa/(\kappa-1)}.$$

On the other hand, Eqn (2.83) yields

$$T(V) = T_0\left(\frac{V}{V_0}\right)^{1-\kappa},$$

therefore

$$p(V) = nRV^{-1}T(V) = nRT_0V_0^{\kappa-1}V^{-\kappa}.$$

(c) Substituting the data into Eqn (2.83) we find that

$$T = 257\,\mathrm{K}.$$

21. (a) The general solution of the differential equation is

$$\psi(x) = A\sin\alpha x + B\cos\alpha x,$$

where A and B are arbitrary constants.

A solution fulfils the boundary conditions if and only if

$$A\sin 0 + B\cos 0 = 0$$

and

$$A\sin\alpha a + B\cos\alpha a = 0.$$

From the first equation $B = 0$, and from the second one

$$\alpha a = \pm n\pi; \qquad n = 1, 2, 3, \ldots \tag{2.84}$$

(notice that $A = 0$ or $n = 0$ would lead to an identically zero solution). Thus, the possible solutions are

$$\psi_n(x) = A_n \sin\frac{n\pi x}{a}; \qquad n = 1, 2, 3, \ldots, \tag{2.85}$$

where A_n is an arbitrary constant. These solutions belong to the values

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}; \qquad n = 1, 2, 3, \ldots,$$

respectively.

(b) On the basis of Eqn (2.85)

$$A_n^2 \int_0^a \sin^2 \frac{n\pi x}{a} \mathrm{d}x = A_n^2 \frac{a}{2} = 1,$$

that is,

$$A_n = \sqrt{\frac{2}{a}}.$$

22. (a) Differentiating the function y defined by

$$\begin{aligned} y_n(x) &= \sum_{i=0}^{n} a_i x^i \qquad (2.86) \\ &= \sum_{i=0}^{n-2} a_i x^i + a_{n-1} x^{n-1} + a_n x^n \end{aligned}$$

we obtain the formulas

$$\begin{aligned} \frac{\mathrm{d}y_n}{\mathrm{d}x}(x) &= \sum_{k=1}^{n} i a_i x^{i-1} \\ \frac{\mathrm{d}^2 y_n}{\mathrm{d}x^2}(x) &= \sum_{i=2}^{n} i(i-1) a_i x^{i-2} = \sum_{i=0}^{n-2} (i+2)(i+1) a_{i+2} x^i \end{aligned}$$

from which

$$\begin{aligned} x \frac{\mathrm{d}y_n}{\mathrm{d}x}(x) &= \sum_{i=1}^{n} i a_i x^i = \sum_{i=0}^{n} i a_i x^i \\ &= \sum_{i=0}^{n-2} i a_i x^i + (n-1) a_{n-1} x^{n-1} + n a_n x^n. \end{aligned}$$

Inserting these formulas into the differential equation we find that

$$\sum_{i=0}^{n-2} \left[(i+2)(i+1) a_{i+2} - 2(i-n) a_i \right] x^i + a_{n-1} x^{n-1} = 0.$$

In the case of $n \geq 2$ this is valid for any possible value of x if and only if

$$a_{n-1} = 0 \qquad (2.87)$$

and

$$a_{i+2} = \frac{2(i-n)}{(i+1)(i+2)} a_i; \qquad i = 0, 1, 2, \ldots, n-2. \tag{2.88}$$

(If this were not true, we would have a polynomial equation for x, which would have only a finite number of roots.) By virtue of Eqns (2.87) and (2.88) all the terms a_i having odd subscripts i vanish if n is even; a_0 and all the terms a_i with even subscripts i will vanish if n is odd.

(b) On the basis of paragraph (22a)

$$\begin{aligned} y_2(x) &= -\frac{a_0}{2}(4x^2 - 2), \\ y_4(x) &= \frac{a_0}{12}(16x^4 - 48x^2 + 12) \end{aligned}$$

and

$$y_6(x) = -\frac{a_0}{120}(64x^6 - 480x^4 + 720x^2 - 120);$$

moreover,

$$y_3(x) = -\frac{a_1}{12}(8x^3 - 12x)$$

and

$$y_5(x) = \frac{a_1}{120}(32x^5 - 160x^3 + 120x).$$

For $n = 0, 1$ we insert Eqn (2.86) and its derivatives directly into the differential equation, which yields

$$y_0(x) = a_0$$

and

$$y_1(x) = a_1 x.$$

(c) Performing the differentiations in the formula of $H_n(x)$ it turns out that for the investigated values of n

$$y_n(x) = C_n H_n(x),$$

that is, $y_n(x)$ and $H_n(x)$ differ from each other in a multiplying factor C_n, which is independent of x. It can be shown that the same is valid for the general case too.

23. (a) In the following summations k does not play a direct role, so – for the sake of simplicity – we do not indicate the dependence of y_n on k. Differentiating the function y_n defined by

$$y_n(x) = \sum_{i=0}^{n} a_i x^i = \sum_{i=1}^{n+1} a_{i-1} x^{i-1} = \sum_{i=1}^{n} a_{i-1} x^{i-1} + a_n x^n$$

we obtain

$$\frac{\mathrm{d}y_n}{\mathrm{d}x}(x) = \sum_{i=1}^{n} i a_i x^{i-1}$$

and

$$\frac{\mathrm{d}^2 y_n}{\mathrm{d}x^2}(x) = \sum_{i=2}^{n} i(i-1) a_i x^{i-2},$$

which lead to

$$x\frac{\mathrm{d}y_n}{\mathrm{d}x}(x) = \sum_{i=1}^{n} i a_i x^i = \sum_{i=1}^{n} (i-1) a_{i-1} x^{i-1} + n a_n x^n$$

and

$$x\frac{\mathrm{d}^2 y_n}{\mathrm{d}x^2}(x) = \sum_{i=2}^{n} i(i-1) a_i x^{i-1} = \sum_{i=1}^{n} i(i-1) a_i x^{i-1}.$$

Utilizing these formulas the investigated differential equation yields

$$\sum_{i=1}^{n} \left[i(i-1)a_i + (k+1)ia_i - (i-1)a_{i-1} + na_{i-1} \right] x^{i-1} = 0. \qquad (2.89)$$

In the case of $n \geq 1$ this is satisfied for all possible values of x if and only if the expressions in the square brackets vanish, that is,

$$a_i = \frac{i-1-n}{i(k+i)} a_{i-1}; \qquad i = 1, 2, 3, \ldots, n. \qquad (2.90)$$

(If there was a non-zero expression in any of the square brackets, Eqn (2.89) would be a non-trivial polynomial equation with a finite number of roots.)

(b) On the basis of Eqn (2.90)

$$y_1(x) = \frac{a_0}{k+1}(k+1-x),$$
$$y_2(x) = \frac{a_0}{(k+1)(k+2)}[(k+1)(k+2) - 2(k+2)x + x^2]$$

and

$$y_3(x) = \frac{a_0}{(k+1)(k+2)(k+3)} \times [(k+1)(k+2)(k+3) - 3(k+2)(k+3)x + 3(k+3)x^2 - x^3].$$

In the case of $n = 0$

$$y_0(x) = a_0,$$

and inserting this directly into the differential equation it turns out that a_0 is arbitrary.

(c) Performing the necessary differentiations in the Rodrigues' formula of the associated Laguerre polynomials it can be seen that for the investigated values of n

$$y_n(x) = C_n L_n^k(x),$$

where C_n is a constant independent of x. It can be proved that this formula is valid for the general case too.

24. (a) Since

$$\hat{\rho}(z) = \frac{z}{\sqrt{\delta\alpha^5\mu}},$$

it follows that

$$\frac{d\hat{\rho}}{dz}(z) = \frac{1}{\sqrt{\delta\alpha^5\mu}}.$$

So from the equation

$$\phi(z) = 1 + \mu\theta(\hat{\rho}(z))$$

we have

$$\begin{aligned}\frac{\mathrm{d}\phi}{\mathrm{d}z}(z) &= \mu\frac{\mathrm{d}\theta}{\mathrm{d}\rho}(\hat{\rho}(z))\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}z}(z)\\ &= \sqrt{\frac{\mu}{\delta\alpha^5}}\frac{\mathrm{d}\theta}{\mathrm{d}\rho}(\hat{\rho}(z))\end{aligned}$$

and

$$\begin{aligned}\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2}(z) &= \sqrt{\frac{\mu}{\delta\alpha^5}}\frac{\mathrm{d}^2\theta}{\mathrm{d}\rho^2}(\hat{\rho}(z))\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}z}(z)\\ &= \frac{1}{\delta\alpha^5}\frac{\mathrm{d}^2\theta}{\mathrm{d}\rho^2}(\hat{\rho}(z)).\end{aligned}$$

By the aid of these formulas and the original differential equation we find that

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2}(z) + \frac{2}{z}\frac{\mathrm{d}\phi}{\mathrm{d}z}(z) + \phi^5(z) = 0.$$

Employing one of the boundary conditions

$$\begin{aligned}\frac{\mathrm{d}\phi}{\mathrm{d}z}(0) &= \sqrt{\frac{\mu}{\delta\alpha^5}}\frac{\mathrm{d}\theta}{\mathrm{d}\rho}(\hat{\rho}(0))\\ &= \sqrt{\frac{\mu}{\delta\alpha^5}}\frac{\mathrm{d}\theta}{\mathrm{d}\rho}(0) = 0,\end{aligned}$$

while the other boundary condition and

$$\hat{\rho}(z^*) = \frac{z^*}{\sqrt{\delta\alpha^5\mu}} = 1$$

yield

$$\phi(z^*) = 1 + \mu\theta(\hat{\rho}(z^*)) = 1 + \mu\theta(1) = 1.$$

(b) If

$$\phi(z) = \left(\frac{a}{z^2+b}\right)^{1/2}$$

then

$$\frac{\mathrm{d}\phi}{\mathrm{d}z}(z) = -\frac{\sqrt{a}z}{(z^2+b)^{3/2}}$$

and

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2}(z) = \frac{\sqrt{a}(2z^2 - b)}{(z^2 + b)^{5/2}},$$

therefore,

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}z^2}(z) + \frac{2}{z}\frac{\mathrm{d}\phi}{\mathrm{d}z}(z) + \phi^5(z) = \frac{\sqrt{a}(a^2 - 3b)}{(z^2 + b)^{5/2}}.$$

For some kind of symmetry let c be the constant for which

$$a = 3c.$$

Then the right-hand side vanishes if and only if

$$b = 3c^2$$

is valid.

(c) The formula

$$\phi(z^*) = \left(\frac{3c}{3c^2 + z^{*2}}\right)^{1/2} = 1$$

gives

$$\frac{3c}{3c^2 + z^{*2}} = 1$$

and

$$3c^2 - 3c + z^{*2} = 0,$$

so

$$c_{1,2} = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - \frac{4\delta\alpha^5\mu}{3}}.$$

25. (a) Since $\hat{u}(x) \leq e^{\hat{u}(x)}$ it follows that

$$\int_0^1 \hat{u}(x)\phi(x)\,\mathrm{d}x \leq \int_0^1 e^{\hat{u}(x)}\phi(x)\,\mathrm{d}x, \tag{2.91}$$

so

$$\int_0^1 \phi(x)\frac{\mathrm{d}^2\hat{u}}{\mathrm{d}x^2}(x)\,\mathrm{d}x = -\delta\int_0^1 e^{\hat{u}(x)}\phi(x)\,\mathrm{d}x \leq -\delta\int_0^1 \hat{u}(x)\phi(x)\,\mathrm{d}x,$$

and using Eqn (1.79) concerning ϕ

$$\int_0^1 \phi(x)\frac{\mathrm{d}^2\hat{u}}{\mathrm{d}x^2}(x)\,\mathrm{d}x \le \frac{\delta}{\lambda}\int_0^1 \hat{u}(x)\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}(x)\,\mathrm{d}x.$$

If we integrate both sides by parts we obtain

$$\begin{aligned}&\left[\phi(x)\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(x)\right]_0^1 - \int_0^1 \frac{\mathrm{d}\phi}{\mathrm{d}x}(x)\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(x)\,\mathrm{d}x\\ &\quad\le \frac{\delta}{\lambda}\left[\frac{\mathrm{d}\phi}{\mathrm{d}x}(x)\hat{u}(x)\right]_0^1 - \frac{\delta}{\lambda}\int_0^1 \frac{\mathrm{d}\phi}{\mathrm{d}x}(x)\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(x)\,\mathrm{d}x,\end{aligned}$$

in which the quantities in the square brackets vanish because of the boundary conditions. Thus, multiplying by -1,

$$\int_0^1 \frac{\mathrm{d}\phi}{\mathrm{d}x}(x)\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(x)\,\mathrm{d}x \ge \frac{\delta}{\lambda}\int_0^1 \frac{\mathrm{d}\phi}{\mathrm{d}x}(x)\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(x)\,\mathrm{d}x. \tag{2.92}$$

Integrating Eqn (1.77) and taking into account the boundary condition concerning the derivative in Eqn (1.78) we obtain

$$\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(x) = -\delta\int_0^x e^{\hat{u}(\xi)}\mathrm{d}\xi < 0, \tag{2.93}$$

and it can be derived similarly that

$$\frac{\mathrm{d}\phi}{\mathrm{d}x}(x) = -\lambda\int_0^x \phi(\xi)\,\mathrm{d}\xi < 0.$$

It follows from the last two equations that the integral in Eqn (2.92) is positive, so the direction of the inequality remains if we divide both sides of Eqn (2.92) by this integral. Thus, a little rearrangement of Eqn (2.92) gives

$$\delta \le \lambda. \tag{2.94}$$

(b) The general solution of Eqn (1.79) is

$$\phi(x) = A\sin\sqrt{\lambda}x + B\cos\sqrt{\lambda}x,$$

where A and B are arbitrary constants. From this

$$\frac{\mathrm{d}\phi}{\mathrm{d}x}(x) = A\sqrt{\lambda}\cos\sqrt{\lambda}x, -B\sqrt{\lambda}\sin\sqrt{\lambda}x.$$

An appropriate solution satisfying the boundary conditions

$$\frac{\mathrm{d}\phi}{\mathrm{d}x}(0) = A\sqrt{\lambda} = 0$$

and

$$\phi(1) = B\cos\sqrt{\lambda} = 0$$

is, for example,

$$\lambda = \frac{\pi^2}{4}; \quad \phi(x) = B\cos\sqrt{\lambda}x.$$

Thus, on the basis of Eqn (2.94) we obtain

$$\delta \le \frac{\pi^2}{4}.$$

(c) Eqn (1.77) is a non-linear second-order differential equation. To solve it we first introduce the function $\hat{v}$ by the definition

$$\hat{v}(u) = \frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(\hat{x}(u)),$$

where $\hat{x}(u)$ denotes the value of the inverse of the unknown function $\hat{u}$. (According to Eqn (2.93) the function $\hat{u}$ is strictly monotonously decreasing, so it has an inverse function.) With this

$$\begin{aligned}\frac{\mathrm{d}\hat{v}}{\mathrm{d}u}(u) &= \frac{\mathrm{d}^2\hat{u}}{\mathrm{d}x^2}(\hat{x}(u))\frac{\mathrm{d}\hat{x}}{\mathrm{d}u}(u) = \frac{\mathrm{d}^2\hat{u}}{\mathrm{d}x^2}(\hat{x}(u))\left[\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(\hat{x}(u))\right]^{-1}\\ &= \frac{\mathrm{d}^2\hat{u}}{\mathrm{d}x^2}(\hat{x}(u))\left[\hat{v}(u)\right]^{-1},\end{aligned}$$

therefore

$$\frac{\mathrm{d}^2\hat{u}}{\mathrm{d}x^2}(\hat{x}(u)) = \frac{\mathrm{d}\hat{v}}{\mathrm{d}u}(u)\hat{v}(u).$$

On the basis of Eqn (1.77)

$$\hat{v}(u)\frac{\mathrm{d}\hat{v}}{\mathrm{d}u}(u) = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}u}\hat{v}^2(u) = -\delta e^u,$$

which gives

$$\hat{v}(u) = \pm\sqrt{2}\sqrt{c - \delta e^u}$$

after integration. Thus,

$$\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(x) = -\sqrt{2}\sqrt{c - \delta e^{\hat{u}(x)}},$$

where c is a positive constant. (We have chosen the negative sign since we have seen that $(\mathrm{d}\hat{u}/\mathrm{d}x)(x)$ is negative.) A rearrangement and an integration yield

$$\int \frac{1}{\sqrt{c - \delta e^{u(x)}}}\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(x) = -\sqrt{2}\int 1\,\mathrm{d}x,$$

from which (with the arbitrary constant d_1)

$$\frac{1}{\sqrt{c}}\ln\left(-\frac{\sqrt{c - \delta e^{\hat{u}(x)}} - \sqrt{c}}{\sqrt{c - \delta e^{\hat{u}(x)}} + \sqrt{c}}\right) = -\sqrt{2}x + d_1,$$

and finally

$$\hat{u}(x) = \ln\left[\frac{-4cde^{-\sqrt{2c}x}}{\delta(1 - de^{-\sqrt{2c}x})^2}\right],$$

where $d = -e^{d_1\sqrt{c}}$. From the boundary condition for the derivative (see Eqn (1.78))

$$\frac{\mathrm{d}\hat{u}}{\mathrm{d}x}(0) = \frac{\sqrt{2c}(d+1)}{d-1} = 0,$$

so

$$d = -1.$$

The other boundary condition leads to the equation

$$\hat{u}(1) = \ln\left[\frac{4ce^{-\sqrt{2c}}}{\delta(1 + e^{-\sqrt{2c}})^2}\right] = 0,$$

which can be rewritten into the form

$$\frac{ce^{-\sqrt{2c}}}{(1+e^{-\sqrt{2c}})^2} = \frac{\delta}{4}. \tag{2.95}$$

The constant c can be obtained by solving this equation. We show that the positive function f defined on the interval $(0, \infty)$ by the formula

$$f(c) = \frac{ce^{-\sqrt{2c}}}{(1+e^{-\sqrt{2c}})^2}$$

has a unique local extremum – a local maximum. From this it follows that Eqn (2.95) has two roots for $(\delta/4) < f(c_{\mathrm{m}})$ but has no roots for $(\delta/4) > f(c_{\mathrm{m}})$ (c_{m} is the point at which the local maximum of f occurs and $f(c_{\mathrm{m}})$ is the height of the maximum). A little calculation shows that the sign and the zeros of the first derivative of f are determined by the expression

$$f_1(c) = e^{\sqrt{2c}}(\sqrt{2} - \sqrt{c}) + \sqrt{2} + \sqrt{c},$$

which changes its sign from positive to negative as $c > 0$ increases. The zeros of f_1 can be determined from the equation

$$g(p) = h(p), \tag{2.96}$$

where

$$p = \sqrt{2c_{\mathrm{m}}}; \quad g(p) = \frac{p-2}{p+2}; \quad h(p) = e^{-p}.$$

In the interval $(0, \infty)$ the function g strictly monotonously increases from -1 to 1, while the function h strictly monotonously decreases from 1 to 0. Thus, the curves of the two functions have exactly one point of intersection, which means that f_1 has exactly one zero. Since f_1 is continuous, it changes its sign at its unique zero. From these properties of f_1 it follows that there is a unique point at which f' becomes zero and changes its sign from positive to negative. This means that f has exactly one local extremum – a local maximum.

(d) Because of the characters of the functions Eqn (2.96) can only be solved by approximate methods. Using mathematical/spreadsheet software

$$c_{\mathrm{m}} = 2.8784\ldots,$$

so

$$f(c_{\mathrm{m}}) = 0.2196\ldots.$$

Let

$$\delta_{\mathrm{c}} = 4f(c_{\mathrm{m}}) = 0.8784\ldots.$$

Then Eqns (1.77) and (1.78) have two solutions for

$$\delta < \delta_{\mathrm{c}}$$

and none for

$$\delta > \delta_{\mathrm{c}}.$$

In the case of $\delta = \delta_{\mathrm{c}}$ there exists one solution. The estimate $\delta \leq (\pi^2/4) = 2.4674\ldots$ obtained in paragraph 25b can be considered relatively rough.

26. From the given function

$$\frac{\partial p}{\partial T}(V, T) = \frac{nR}{V}$$

and

$$\frac{p(V, T)}{T} = \frac{nR}{V},$$

so p is really a solution of the differential equation. At the same time let f be any function for which $f(V) > 0$ in the domain of definition of Eqn (1.81). Then – using similar considerations as earlier – we find that

$$p(V, T) = \frac{nRT}{f(V)}$$

also is a positive solution of the differential equation investigated. Thus, the laws of thermodynamics do not determine fully the form of the perfect-gas equation.

27. (a) Using the notation

$$\beta^2 + \gamma^2 = \frac{2mE}{\hbar^2} \tag{2.97}$$

the equation to be solved is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -(\beta^2 + \gamma^2)\psi. \tag{2.98}$$

By the insertion of the formulas

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\mathrm{d}^2X}{\mathrm{d}x^2}Y; \qquad \frac{\partial^2\psi}{\partial y^2} = \frac{\mathrm{d}^2Y}{\mathrm{d}y^2}X$$

Eqn (2.98) can be written into the form

$$Y\left[\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + \beta^2X\right] + X\left[\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} + \gamma^2Y\right] = 0$$

whose abbreviated variant is

$$Y(y)F(x) + X(x)G(y) = 0. \tag{2.99}$$

Here $F(x)$ and $G(y)$ denote the formulas in the first and second square brackets on the left-hand side, respectively. If ψ is a not identically zero solution of the form Eqn (1.82) then there exists an $\bar{x}$ for which $X(\bar{x}) \neq 0$, and so, according to Eqn (2.99),

$$G(y) = -\frac{F(\bar{x})}{X(\bar{x})}Y(y) = c_1Y(y).$$

By a similar reasoning we obtain

$$F(x) = -\frac{G(\bar{y})}{Y(\bar{y})}X(x) = c_2X(x).$$

Inserting the latter two formulas into Eqn (2.99) and then substituting the values $\bar{x}$ and $\bar{y}$ we find that

$$(c_1 + c_2)X(\bar{x})Y(\bar{y}) = 0,$$

which implies

$$c_1 = -c_2.$$

Assume that c_1 is non-negative, and let $c^2 = c_1$. (If our assumption were not true then c_2 would be non-negative, and this case can be treated similarly.) With this notation

$$\frac{\mathrm{d}^2X}{\mathrm{d}x^2} + \beta^2X = -c^2X$$

and

$$\frac{d^2Y}{dy^2} + \gamma^2 Y = c^2 Y,$$

that is, in rearranged forms

$$\frac{d^2X}{dx^2} = -\beta_1^2 X \tag{2.100}$$

and

$$\frac{d^2Y}{dy^2} = -(\gamma^2 - c^2)Y, \tag{2.101}$$

where

$$\beta_1^2 = \beta^2 + c^2.$$

The possible cases are as follows:

i. $\beta_1^2 > 0, \gamma_1^2 = \gamma^2 - c^2 > 0$. Then on the basis of the general solutions of Eqn (2.100) and Eqn (2.101)

$$\psi(x,y) = (A\sin\beta_1 x + B\cos\beta_1 x)(C\sin\gamma_1 y + D\cos\gamma_1 y).$$

From the boundary condition

$$\psi(0,y) = B(C\sin\gamma_1 y + D\cos\gamma_1 y) = 0$$

it follows that $B = 0$ since $C = D = 0$ would lead to an identically zero solution. The boundary condition

$$\psi(x,0) = AD\sin\beta_1 x = 0$$

gives $D = 0$ ($A = 0$ would lead to an identically zero solution). The boundary condition

$$\psi(a,y) = AC\sin\beta_1 a\sin\gamma_1 y = 0$$

is fulfilled if and only if

$$\beta_1 a = k\pi; \qquad k = \pm 1, \pm 2, \pm 3, \ldots.$$

($C = 0$ or $k = 0$ would yield an identically zero solution so they are excluded.) Finally, the boundary condition

$$\psi(x, b) = AC \sin \gamma_1 b \sin \beta_1 x = 0$$

implies

$$\gamma_1 b = l\pi; \qquad l = \pm 1, \pm 2, \pm 3, \ldots,$$

and

$$\alpha^2 = \beta^2 + \gamma^2 = \beta_1^2 + \gamma_1^2 = \left(\frac{k^2}{a^2} + \frac{l^2}{b^2}\right)\pi^2.$$

Using the formulas derived so far the solution of the problem is

$$\psi_{kl}(x, y) = N \sin \frac{k\pi}{a} x \sin \frac{l\pi}{b} y; \qquad k, l = 1, 2, 3, \ldots \tag{2.102}$$

with

$$E_{kl} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{k^2}{a^2} + \frac{l^2}{b^2}\right); \qquad k, l = 1, 2, 3, \ldots. \tag{2.103}$$

Mathematically N is an arbitrary constant, but on the basis of the physical meaning of ψ its value can be fixed by the equation

$$\int_0^b \int_0^a N^2 \sin^2 \frac{k\pi}{a} x \sin^2 \frac{l\pi}{b} y \, \mathrm{d}x \, \mathrm{d}y = 1,$$

which yields

$$N = \frac{2}{\sqrt{ab}}.$$

ii. $\beta_1^2 > 0, \gamma_1^2 = \gamma^2 - c^2 = 0$. Now the general solutions of Eqns (2.100) and (2.101) are

$$X(x) = A \sin \beta_1 x + B \cos \beta_1 x$$

and

$$Y(y) = Cy + D,$$

respectively, so

$$\psi(x,y) = (A\sin\beta_1 x + B\cos\beta_1 x)(Cy + D).$$

However, it can be shown by an argumentation similar to the one applied in paragraph 27(a)i that this solution does not obey all the boundary conditions for any choice of the constants A, B, C and D.

iii. $\beta_1^2 > 0$, $\gamma_1^2 = -(\gamma^2 - c^2) > 0$. In this case the general solutions of Eqns (2.100) and (2.101) are

$$X(x) = A\sin\beta_1 x + B\cos\beta_1 x$$

and

$$Y(y) = Ce^{\gamma_1 y} + De^{-\gamma_1 y},$$

respectively, so

$$\psi(x,y) = (A\sin\beta_1 x + B\cos\beta_1 x)(Ce^{\gamma_1 y} + De^{-\gamma_1 y}).$$

After some calculation it turns out that – independently of the values of the constants A, B, C and D – this solution cannot obey all the boundary conditions, either.

The case $\beta_1^2 = 0$ and $\gamma_1^2 = \gamma^2 - c^2 = 0$ cannot occur since it contradicts to the condition $\alpha^2 > 0$. The two members of the formula pair $\beta_1^2 = 0$ and $\gamma_1^2 = -(\gamma^2 - c^2) > 0$ contradict to each other. The case $\beta_1^2 = 0$ and $\gamma_1^2 = \gamma^2 - c^2 > 0$ can be treated according to paragraph 27(a)ii, and gives the same result.

(b) In the case of $a = b$ Eqn (2.103) becomes

$$E_{kl} = \frac{\hbar^2\pi^2}{2ma^2}(k^2 + l^2); \quad k,l = 1,2,3,\ldots,$$

which means that $E_{kl} = E_{lk}$. Thus, the functions ψ_{kl} and ψ_{lk} given by Eqn (2.102) will now belong to the same value $E = E_{kl} = E_{lk}$.

28. Using the notation

$$\hat{z}(x,t) = \frac{x}{2\sqrt{Dt}}$$

we have

$$c(x,t) = f(\hat{z}(x,t))$$

so

$$\frac{\partial c}{\partial t}(x,t) = \frac{\mathrm{d}f}{\mathrm{d}z}(\hat{z}(x,t))\frac{\partial \hat{z}}{\partial t}(x,t) = -\frac{\mathrm{d}f}{\mathrm{d}z}(\hat{z}(x,t))\frac{x}{4t\sqrt{Dt}}$$

and

$$\frac{\partial^2 c}{\partial x^2}(x,t) = \frac{\mathrm{d}^2 f}{\mathrm{d}z^2}(\hat{z}(x,t))\left[\frac{\partial \hat{z}}{\partial x}(x,t)\right]^2.$$

After the substitution of these formulas Eqn (1.83) takes the form

$$\frac{\mathrm{d}^2 f}{\mathrm{d}z^2}(z) + 2z\frac{\mathrm{d}f}{\mathrm{d}z}(z) = 0; \quad -\infty < z < \infty, \tag{2.104}$$

where $z = \hat{z}(x,t)$. Introducing the new unknown

$$g(z) = \frac{\mathrm{d}f}{\mathrm{d}z}(z)$$

Eqn (2.104) can be reduced to the first-order equation

$$\frac{\mathrm{d}g}{\mathrm{d}z}(z) + 2zg(z) = 0; \quad -\infty < z < \infty$$

whose solution – using the method of separation of variables – is

$$g(z) = g(0)e^{-z^2}.$$

With this solution

$$\begin{aligned} f(z) &= f(0) + \int_0^z g(\xi)\,\mathrm{d}\xi = f(0) + \frac{\mathrm{d}f}{\mathrm{d}z}(0)\int_0^z e^{-\xi^2}\,\mathrm{d}\xi \\ &= f(0) + \frac{\sqrt{\pi}}{2}\frac{\mathrm{d}f}{\mathrm{d}z}(0)\mathrm{erf}(z), \end{aligned}$$

where the error function, erf, is defined by

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-\xi^2}\,\mathrm{d}\xi.$$

29. (a) Employing the new variable given in the problem

$$c(x,t) = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty} \phi(x - \xi\sqrt{4Dt})e^{-\xi^2}\,\mathrm{d}\xi.$$

i. From the initial condition we obtain

$$\phi(x-\xi\sqrt{4Dt}) = \begin{cases} c_1; & \xi > \frac{x}{\sqrt{4Dt}}, \\ c_2; & \xi \leq \frac{x}{\sqrt{4Dt}}, \end{cases}$$

with which

$$c(x,t) = \frac{1}{\sqrt{\pi}}\left[c_2\int_{-\infty}^{\frac{x}{\sqrt{4Dt}}} e^{-\xi^2}\,\mathrm{d}\xi + c_1\int_{\frac{x}{\sqrt{4Dt}}}^{\infty} e^{-\xi^2}\,\mathrm{d}\xi\right].$$

Applying the additional transformations

$$\begin{aligned} c(x,t) = \frac{1}{\sqrt{\pi}}\Bigg[&c_2\int_{-\infty}^{0} e^{-\xi^2}\,\mathrm{d}\xi + c_2\int_{0}^{\frac{x}{\sqrt{4Dt}}} e^{-\xi^2}\,\mathrm{d}\xi \\ &+ c_1\int_{\frac{x}{\sqrt{4Dt}}}^{0} e^{-\xi^2}\,\mathrm{d}\xi + c_1\int_{0}^{\infty} e^{-\xi^2}\,\mathrm{d}\xi\Bigg] \\ c(x,t) = \frac{1}{\sqrt{\pi}}\Bigg[&c_2\frac{\sqrt{\pi}}{2} + c_2\int_{0}^{\frac{x}{\sqrt{4Dt}}} e^{-\xi^2}\,\mathrm{d}\xi \\ &- c_1\int_{0}^{\frac{x}{\sqrt{4Dt}}} e^{-\xi^2}\,\mathrm{d}\xi + c_1\frac{\sqrt{\pi}}{2}\Bigg] \end{aligned}$$

we can introduce the function erf, and after some calculation

$$c(x,t) = \frac{c_2+c_1}{2} + \frac{c_2-c_1}{2}\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right). \tag{2.105}$$

ii. From the initial condition

$$\phi(x-\xi\sqrt{4Dt}) = \begin{cases} c_0; & \frac{x-a}{\sqrt{4Dt}} \leq \xi \leq \frac{x+a}{\sqrt{4Dt}}, \\ 0; & \xi < \frac{x-a}{\sqrt{4Dt}},\ \xi > \frac{x+a}{\sqrt{4Dt}}, \end{cases}$$

and employing this

$$c(x,t) = \frac{c_0}{\sqrt{\pi}}\int_{\frac{x-a}{\sqrt{4Dt}}}^{\frac{x+a}{\sqrt{4Dt}}} e^{-\xi^2}\,\mathrm{d}\xi.$$

In order to introduce the function erf we split the integral as

$$c(x,t)=\frac{c_0}{\sqrt{\pi}}\left[-\int_0^{\frac{x-a}{\sqrt{4Dt}}} e^{-\xi^2}\,\mathrm{d}\xi+\int_0^{\frac{x+a}{\sqrt{4Dt}}} e^{-\xi^2}\,\mathrm{d}\xi\right],$$

and finally we obtain

$$c(x,t)=\frac{c_0}{2}\left[\operatorname{erf}\left(\frac{x+a}{\sqrt{4Dt}}\right)-\operatorname{erf}\left(\frac{x-a}{\sqrt{4Dt}}\right)\right].$$

iii. Using the initial condition

$$\phi(x-\xi\sqrt{4Dt})=\begin{cases} c_0\left(1-\frac{|x-\xi\sqrt{4Dt}|}{a}\right); & \frac{x-a}{\sqrt{4Dt}}\le\xi\le\frac{x+a}{\sqrt{4Dt}},\\ 0; & \xi<\frac{x-a}{\sqrt{4Dt}},\ \xi>\frac{x+a}{\sqrt{4Dt}},\end{cases}$$

so

$$\begin{aligned} c(x,t)&=\frac{c_0}{\sqrt{\pi}}\int_{\frac{x-a}{\sqrt{4Dt}}}^{\frac{x+a}{\sqrt{4Dt}}}\left(1-\frac{|x-\xi\sqrt{4Dt}|}{a}\right)e^{-\xi^2}\,\mathrm{d}\xi\\ &=\frac{c_0}{\sqrt{\pi}}\int_{\frac{x-a}{\sqrt{4Dt}}}^{\frac{x+a}{\sqrt{4Dt}}} e^{-\xi^2}\,\mathrm{d}\xi-\frac{c_0}{a\sqrt{\pi}}\int_{\frac{x-a}{\sqrt{4Dt}}}^{\frac{x+a}{\sqrt{4Dt}}}|x-\xi\sqrt{4Dt}|e^{-\xi^2}\,\mathrm{d}\xi. \end{aligned}$$

Like to the previous paragraphs we split the integrals into appropriate parts, and introduce the function erf. Finally, we find that

$$\begin{aligned} c(x,t)=\frac{c_0}{2}\Bigg\{&\left(1+\frac{x}{a}\right)\operatorname{erf}\left(\frac{x+a}{\sqrt{4Dt}}\right)\\ &-\left(1-\frac{x}{a}\right)\operatorname{erf}\left(\frac{x-a}{\sqrt{4Dt}}\right)\\ &-\frac{2x}{a}\operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right)\\ &-\sqrt{\frac{4Dt}{\pi a^2}}\left[2e^{-\frac{x^2}{4Dt}}-e^{-\frac{(x-a)^2}{4Dt}}-e^{-\frac{(x+a)^2}{4Dt}}\right]\Bigg\}. \end{aligned} \quad (2.106)$$

(In the calculations always attach the signs required by the integration limits to the absolute values.)

(b) The key element is the differentiation of the function erf:

$$\frac{\partial}{\partial x}\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) = \frac{2}{\sqrt{\pi}}e^{-(x/\sqrt{4Dt})^2}\frac{\partial}{\partial x}\frac{x}{\sqrt{4Dt}}$$
$$= \frac{1}{\sqrt{\pi Dt}}e^{-(x/\sqrt{4Dt})^2} \tag{2.107}$$

and

$$\frac{\partial}{\partial t}\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) = \frac{2}{\sqrt{\pi}}e^{-(x/\sqrt{4Dt})^2}\frac{\partial}{\partial t}\frac{x}{\sqrt{4Dt}}$$
$$= -\frac{x}{t\sqrt{4\pi Dt}}e^{-(x/\sqrt{4Dt})^2}. \tag{2.108}$$

Using these formulas we obtain

i.

$$\frac{\partial c}{\partial t}(x,t) = \frac{xe^{-(x/\sqrt{4Dt})^2}(c_1 - c_2)}{4t\sqrt{\pi Dt}},$$

$$\frac{\partial^2 c}{\partial x^2}(x,t) = \frac{xe^{-(x/\sqrt{4Dt})^2}(c_1 - c_2)}{4Dt\sqrt{\pi Dt}} \quad \text{and}$$

ii.

$$\frac{\partial c}{\partial t}(x,t) = \frac{c_0}{4t\sqrt{\pi Dt}}\left[(x-a)e^{-((x-a)/\sqrt{4Dt})^2} - (x+a)e^{-((x+a)/\sqrt{4Dt})^2}\right],$$

$$\frac{\partial^2 c}{\partial x^2}(x,t) = \frac{c_0}{4Dt\sqrt{\pi Dt}}\left[(x-a)e^{-((x-a)/\sqrt{4Dt})^2} - (x+a)e^{-((x+a)/\sqrt{4Dt})^2}\right].$$

Thus, in both cases

$$\frac{\partial c}{\partial t}(x,t) = D\frac{\partial^2 c}{\partial x^2}(x,t). \tag{2.109}$$

(c) We investigate only one case, the others can be treated similarly. If $-a < x_0 < a$ and $x_0 > 0$ then, on the basis of Eqn (2.106),

$$\lim_{t\to 0} g(t) = \frac{c_0}{2}\left[\left(1 + \frac{x_0}{a}\right)\mathrm{erf}(\infty)\right.$$
$$\left. - \left(1 - \frac{x_0}{a}\right)\mathrm{erf}(-\infty) - \frac{2x_0}{a}\mathrm{erf}(\infty)\right].$$

Because of

$$\operatorname{erf}(\pm\infty) = \lim_{z\to\pm\infty} \operatorname{erf}(z) = \pm 1$$

the final formula can be written as

$$\lim_{t\to 0} g(t) = c_0\left(1 - \frac{x_0}{a}\right) = c_0\left(1 - \frac{|x_0|}{a}\right).$$

Let us investigate the point $x_0 = 0$ too, at which the initial condition belonging to Eqn (2.105) is discontinuous. Here

$$\lim_{t\to\infty} g(t) = \frac{c_1 + c_2}{2},$$

so the assertion is not valid.

30. (a)

$$c(x,t) = \frac{c_0}{\sqrt{4D\pi t}} \int_0^\infty \left[e^{-\frac{(x-\alpha)^2}{4Dt}} - e^{-\frac{(x+\alpha)^2}{4Dt}} \mathrm{d}\alpha \right]$$

and

$$\begin{aligned}\int_0^\infty e^{-\frac{(x-\alpha)^2}{4Dt}} \mathrm{d}\alpha &= \sqrt{4Dt} \int_{-\infty}^{\frac{x}{\sqrt{4Dt}}} e^{-\xi^2}\, \mathrm{d}\xi \\ &= \sqrt{D\pi t}\left[\operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right) + 1\right],\end{aligned}$$

moreover,

$$\begin{aligned}\int_0^\infty e^{-\frac{(x+\alpha)^2}{4Dt}} \mathrm{d}\alpha &= \sqrt{4Dt} \int_{\frac{x}{\sqrt{4Dt}}}^{\infty} e^{-\eta^2} \mathrm{d}\eta \\ &= \sqrt{D\pi t}\left[1 - \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right)\right],\end{aligned}$$

therefore

$$c(x,t) = c_0 \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right). \tag{2.110}$$

(b) Using Eqns (2.107) and (2.108)

$$\begin{aligned}\frac{\partial c}{\partial t}(x,t) &= -\frac{c_0 x e^{-(x/\sqrt{4Dt})^2}}{2t\sqrt{\pi D t}}, \\ \frac{\partial c}{\partial x}(x,t) &= \frac{c_0}{\sqrt{\pi D t}} e^{-(x^2/4Dt)}\end{aligned} \tag{2.111}$$

and

$$\frac{\partial^2 c}{\partial x^2}(x,t) = -\frac{c_0 x e^{-(x/\sqrt{4Dt})^2}}{2Dt\sqrt{\pi Dt}},$$

so Eqn (2.109) is valid.

(c) Using Eqn (2.111) the time T elapsed from the start of the experiment satisfies

$$\frac{\partial c}{\partial x}(0,T) = \frac{c_0}{\sqrt{\pi DT}} = \gamma,$$

from which

$$T = \frac{c_0^2}{\pi D\gamma^2}.$$

31. (a) Inserting the equations

$$\frac{\partial c}{\partial t} = \frac{\partial u}{\partial t} f + \frac{\mathrm{d}f}{\mathrm{d}t} u$$

and

$$\frac{\partial^2 c}{\partial x^2} = \frac{\partial^2 u}{\partial x^2} f$$

into Eqn (1.88) and employing Eqn (1.91) we find that

$$\left(\frac{\mathrm{d}f}{\mathrm{d}t} - kb_0 f\right) u = 0; \quad t > 0; \quad 0 < x < L,$$

which is definitely valid if

$$\frac{\mathrm{d}f}{\mathrm{d}t} - kb_0 f = 0; \quad t \geq 0,$$

that is, if

$$f(t) = Ce^{kb_0 t}; \quad t \geq 0,$$

where C is an arbitrary constant. For simplicity, let $C = 1$. Then it follows from

$$c(x,t) = e^{kb_0 t} u(x,t) \tag{2.112}$$

that

$$c(x,0) = u(x,0) = c_0,$$

moreover,

$$c(0,t) = e^{kb_0 t}u(0,t) = 0$$

and

$$c(L,t) = e^{kb_0 t}u(L,t) = 0,$$

from which

$$u(0,t) = u(L,t) = 0.$$

(b) According to the method of separation of variables we insert

$$u(x,t) = X(x)T(t)$$

into the differential equation, and obtain

$$\frac{1}{D}X(x)T'(t) = X''(x)T(t). \tag{2.113}$$

As u is a not identically zero solution, there exist an $\bar{x}$ and a $\bar{t}$ for which $X(\bar{x}) \neq 0$ and $T(\bar{t}) \neq 0$. As Eqn (2.113) is valid for all the possible pairs (x,t), we may write that

$$\begin{aligned} \frac{1}{D}\frac{T'(\bar{t})}{T(\bar{t})}X(x) &= X''(x), \\ \frac{1}{D}T'(t) &= \frac{X''(\bar{x})}{X(\bar{x})}T(t) \end{aligned}$$

and

$$\frac{1}{D}\frac{T'(\bar{t})}{T(\bar{t})} = \frac{X''(\bar{x})}{X(\bar{x})}.$$

Thus, T and X must fulfil the equations

$$T'(t) = DqT(t)$$

and

$$X''(x) = qX(x)$$

where $q = (1/D)(T'(\bar{t})/T(\bar{t}))$. If $q > 0$, unbounded solutions occur, which is impossible. If $q = 0$, the solution of the second differential equation is a linear function, which cannot obey the boundary conditions.

Thus, q must be negative, and with the notation $q = -\lambda^2$ the appropriate solutions will be

$$T(t) = Ce^{-\lambda^2 Dt}$$

and

$$X(x) = P \sin \lambda x + Q \cos \lambda x.$$

However,

$$X(0) = X(L) = 0$$

must be simultaneously valid so

$$Q = 0 \text{ and } \lambda = \frac{n\pi}{L}; \qquad n = \pm 1, \pm 2, \pm 3, \ldots$$

(the value $n = 0$ is excluded since it would yield an identically zero solution). Thus,

$$u_n(x,t) = A_n e^{-(n^2\pi^2 D/L^2)t} \sin \frac{n\pi}{L} x; \qquad n = 1, 2, 3, \ldots,$$

where A_n is an arbitrary constant.

(c) Using the coefficients

$$A_n = \frac{2}{L} \int_0^L c_0 \sin \frac{n\pi}{L} \xi \, \mathrm{d}\xi = \frac{2c_0}{n\pi}(1 - \cos n\pi); \qquad n = 1, 2, 3, \ldots$$

obtained from the Fourier expansion of the initial condition we obtain

$$u(x,t) = \frac{2c_0}{\pi} \sum_{n=1}^{\infty} \frac{(1 - \cos n\pi)}{n} e^{-\frac{n^2\pi^2 D}{L^2} t} \sin \frac{n\pi}{L} x.$$

(d) On the basis of Eqn (2.112)

$$c(x,t) = \frac{2c_0}{\pi} \sum_{n=1}^{\infty} \frac{(1 - \cos n\pi)}{n} e^{\left(kb_0 - \frac{n^2\pi^2 D}{L^2}\right)t} \sin \frac{n\pi}{L} x.$$

In the case of

$$L > \pi \sqrt{\frac{D}{kb_0}}$$

the exponent in the non-zero first term is positive, which makes c unbounded as a function of t.

32. (a) Let $\xi = \hat{\xi}(x,t) = x + vt$. Differentiating

$$c(x,t) = f(\hat{\xi}(x,t))$$

we obtain

$$\frac{\partial c}{\partial t}(x,t) = \frac{\mathrm{d}f}{d\xi}(\hat{\xi}(x,t))\frac{\partial\hat{\xi}}{\partial t}(x,t) = \frac{\mathrm{d}f}{\mathrm{d}\xi}(\hat{\xi}(x,t))v,$$
$$\frac{\partial c}{\partial x}(x,t) = \frac{\mathrm{d}f}{\mathrm{d}\xi}(\hat{\xi}(x,t))\frac{\partial\hat{\xi}}{\partial x}(x,t) = \frac{\mathrm{d}f}{\mathrm{d}\xi}(\hat{\xi}(x,t))$$

and

$$\frac{\partial^2 c}{\partial x^2}(x,t) = \frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2}(\hat{\xi}(x,t))\frac{\partial\hat{\xi}}{\partial x}(x,t) = \frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2}(\hat{\xi}(x,t)).$$

Inserting these formulas into the differential equation we arrive at the equation

$$D\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2}(\xi) - v\frac{\mathrm{d}f}{\mathrm{d}\xi}(\xi) + kb_0 f(\xi) = 0; \qquad -\infty < \xi < \infty. \qquad (2.114)$$

(b) Inserting

$$f(\xi) = Pe^{\lambda_1\xi} + Qe^{\lambda_2\xi}$$

into Eqn (2.114) we find that f satisfies the differential equation if and only if

$$\lambda_{1,2} = \frac{v \pm \sqrt{v^2 - 4Dkb_0}}{2D}.$$

The solution tends to the required limits if and only if $\lambda_{1,2} < 0$. But $\lambda_{1,2} < 0$ occurs if and only if $v < 0$ and

$$|v| \geq 2\sqrt{Dkb_0}.$$

33. Substituting the expression of $f(\xi)$ and the formulas

$$f'(\xi) = \frac{2ABe^{-B\xi}}{(1 + Ae^{-B\xi})^3}$$

and

$$f''(\xi) = 2ABe^{-B\xi}\frac{2ABe^{-B\xi} - B}{(1 + Ae^{-B\xi})^4}$$

into the differential equation we find that

$$A^2(4B^2 - 2Bv + 1)e^{-B\xi} + (2A - 2ABv - 2AB^2) = 0,$$

which – taking into account $A > 0$ and $B \neq 0$ – is satisfied for any possible value of ξ if and only if the expressions in the two round brackets vanish. From the two equations obtained in this way

$$B = \pm\frac{\sqrt{6}}{6}; \qquad v = \pm\frac{5\sqrt{6}}{6},$$

but – because of the boundary conditions – only the + sign can be accepted.

34. Inserting the expression of $f(\xi)$ and the formulas

$$f'(\xi) = \frac{kKe^{-k\xi}}{(1 + Ke^{-k\xi})^2}$$

and

$$f''(\xi) = \frac{k^2Ke^{-k\xi}(Ke^{-k\xi} - 1)}{(1 + Ke^{-k\xi})^3}$$

into the differential equation we obtain the equation

$$kK^2e^{-k\xi}(2k + v) + K(1 - 2k^2 + kv) = 0$$

which – because of $K > 0$ and $k \neq 0$ – is fulfilled if and only if the expressions in the two round brackets vanish. This results in two equations, from which

$$k = \pm\frac{1}{2}; \qquad v = \mp 1.$$

Because of the boundary conditions we must choose the lower signs in the formula.

35. (a) The function $\hat{q}$ in Eqn (1.97) is strictly monotonous and so invertible. Denote the value of the inverse function by $\hat{\xi}(q)$. Differentiating the function $\hat{p}$ defined by

$$\hat{p}(q) = -\frac{\mathrm{d}\hat{q}}{\mathrm{d}\xi}(\hat{\xi}(q))$$

we find that

$$\frac{\mathrm{d}\hat{p}}{\mathrm{d}q}(q) = -\frac{\mathrm{d}^2\hat{q}}{\mathrm{d}\xi^2}(\hat{\xi}(q))\frac{\mathrm{d}\hat{\xi}}{\mathrm{d}q}(q) = -\frac{\mathrm{d}^2\hat{q}}{\mathrm{d}\xi^2}(\hat{\xi}(q))\left[\frac{\mathrm{d}\hat{q}}{\mathrm{d}\xi}((q))\right]^{-1}$$
$$= \frac{\mathrm{d}^2\hat{q}}{\mathrm{d}\xi^2}(\hat{\xi}(q))\frac{1}{\hat{p}(q)},$$

and using this in Eqn (1.97) we obtain Eqn (1.100). The boundary conditions in Eqn (1.101) are obviously satisfied.

(b) Inserting the expression of $\hat{p}(q)$ and the formula

$$\frac{\mathrm{d}\hat{p}}{\mathrm{d}q}(q) = \frac{\sqrt{2}}{2}(1-2q)$$

into Eqn (1.100) a rearrangement yields

$$v = \frac{\sqrt{2}}{2}(1-2a).$$

On the basis of the definition of $\hat{p}$ we obtain the function $\hat{q}$ by the solution of the differential equation

$$-\frac{\mathrm{d}\hat{q}}{\mathrm{d}\xi} = \frac{\sqrt{2}}{2}\hat{q}(1-\hat{q}).$$

Using the method of separation of variables

$$\hat{q}(\xi) = \frac{1}{1+Ce^{\frac{\sqrt{2}}{2}\xi}}; \qquad C > 0.$$

This satisfies the boundary conditions in Eqn (1.98) while its derivative satisfies the conditions in Eqn (1.99).

36. Let $\hat{r}(x,y,z) = \sqrt{x^2+y^2+z^2} = r$. In the case of spherical symmetry the first and the second derivatives with respect to x can be described by the formulas

$$\frac{\partial f}{\partial x}(r) = \frac{\mathrm{d}f}{\mathrm{d}r}(r)\frac{\partial \hat{r}}{\partial x}(x,y,z) = \frac{\mathrm{d}f}{\mathrm{d}r}(r)\frac{x}{r}$$

and

$$\frac{\partial^2 f}{\partial x^2}(r) = \frac{\mathrm{d}^2 f}{\mathrm{d}r^2}(r)\frac{x^2}{r^2} + \frac{\mathrm{d}f}{\mathrm{d}r}(r)\frac{r-(x^2/r)}{r^2}.$$

A completely similar derivation yields

$$\frac{\partial^2 f}{\partial y^2}(r) = \frac{\mathrm{d}^2 f}{\mathrm{d}r^2}(r)\frac{y^2}{r^2} + \frac{\mathrm{d}f}{\mathrm{d}r}(r)\frac{r-(y^2/r)}{r^2}$$

and

$$\frac{\partial^2 f}{\partial z^2}(r) = \frac{\mathrm{d}^2 f}{\mathrm{d}r^2}(r)\frac{z^2}{r^2} + \frac{\mathrm{d}f}{\mathrm{d}r}(r)\frac{r-(z^2/r)}{r^2}.$$

Adding the second derivatives with respect to x, y and z we obtain

$$\Delta f(r) = \frac{\partial^2 f}{\partial x^2}(r) + \frac{\partial^2 f}{\partial y^2}(r) + \frac{\partial^2 f}{\partial z^2}(r) = \frac{\mathrm{d}^2 f}{\mathrm{d}r^2}(r) + \frac{2}{r}\frac{\mathrm{d}f}{\mathrm{d}r}(r),$$

so the equation to be solved is

$$\frac{\mathrm{d}^2 f}{\mathrm{d}r^2}(r) + \frac{2}{r}\frac{\mathrm{d}f}{\mathrm{d}r}(r) = \kappa^2 f(r). \tag{2.115}$$

Introducing the new unknown $g(r) = rf(r)$ we have

$$\frac{\mathrm{d}g}{\mathrm{d}r}(r) = f(r) + r\frac{\mathrm{d}f}{\mathrm{d}r}(r)$$

and

$$\frac{\mathrm{d}^2 g}{\mathrm{d}r^2}(r) = r\frac{\mathrm{d}^2 f}{\mathrm{d}r^2}(r) + 2\frac{\mathrm{d}f}{\mathrm{d}r}(r),$$

so Eqn (2.115) takes the form

$$\frac{\mathrm{d}^2 g}{\mathrm{d}r^2}(r) = \kappa^2 g(r).$$

From the general solution

$$g(r) = Ae^{\kappa r} + Be^{-\kappa r}$$

it follows that

$$f(r) = \frac{g(r)}{r} = A\frac{e^{\kappa r}}{r} + B\frac{e^{-\kappa r}}{r},$$

where A and B are arbitrary constants. According to L'Hospital's rule

$$\lim_{r\to\infty}\frac{e^{\kappa r}}{r} = \lim_{r\to\infty}\frac{\kappa e^{\kappa r}}{1} = \infty$$

and

$$\lim_{r\to\infty} \frac{e^{-\kappa r}}{r} = 0,$$

so the desired limit occurs if and only if $A = 0$. This gives the solution

$$f(r) = B\frac{e^{-\kappa r}}{r}.$$

2.6 OTHER PROBLEMS

1. Let

$$\psi = \theta(r) - \omega t.$$

(a) Then

$$\frac{\partial \mathbf{R}}{\partial t}(r,\, t) = r\omega \sin\psi \mathbf{i} - r\omega \cos\psi \mathbf{j},$$

and a tangent vector of the curve (pointing towards the direction corresponding to the increase of r) is

$$\frac{\partial \mathbf{R}}{\partial r}(r,\, t) = \left[\cos\psi - r\theta'(r)\sin\psi\right]\mathbf{i} + \left[\sin\psi + r\theta'(r)\cos\psi\right]\mathbf{j}.$$

For the normal unit vector

$$\mathbf{e}_n(r,\, t) = A(r,\, t)\mathbf{i} + B(r,\, t)\mathbf{j},$$

which is perpendicular to the tangent vector,

$$\left[\cos\psi - r\theta'(r)\sin\psi\right]A(r,\, t) + \left[\sin\psi + r\theta'(r)\cos\psi\right]B(r,\, t) = 0$$

because of the perpendicularity and

$$A^2(r,\, t) + B^2(r,\, t) = 1$$

because of the unit length. From the latter two equations

$$A(r,\, t) = \pm\frac{\sin\psi + r\theta'(r)\cos\psi}{\sqrt{1 + r^2\theta'^2(r)}}$$

and

$$B(r,t) = \mp \frac{\cos\psi - r\theta'(r)\sin\psi}{\sqrt{1 + r^2\theta'^2(r)}}.$$

So the component of the vector $(\partial\mathbf{R}/\partial t)(r,t)$ in the direction of $\mathbf{e}_n(r,t)$ is

$$N(r,t) = \left(\frac{\partial\mathbf{R}}{\partial t}(r,t), \mathbf{e}_n(r,t)\right) = \pm\frac{r\omega}{\sqrt{1 + r^2\theta'^2(r)}},$$

and this is independent of the variable t. Tyson and Keener [61] solved the approximate "eikonal equation"

$$N(r,t) = c$$

(where c is constant) for $\theta'(r)$, and determined how θ depends on r. With this they have given the concrete equation of the spiral reaction fronts investigated. See [61] for the details.

(b) The necessary derivatives are as follows:

$$\begin{aligned} X_r'(r,t) &= \cos\psi - r\theta'(r)\sin\psi, \\ X_r''(r,t) &= -2\theta'(r)\sin\psi - r\theta'^2(r)\cos\psi - r\theta''(r)\sin\psi, \\ Y_r'(r,t) &= \sin\psi + r\theta'(r)\cos\psi \end{aligned}$$

and

$$Y_r''(r,t) = 2\theta'(r)\cos\psi - r\theta'^2(r)\sin\psi + r\theta''(r)\cos\psi.$$

Then we insert these formulas into the equation given in the problem and obtain

$$\kappa(r,t) = \frac{2\theta'(r) + r\theta''(r) + r^2\theta'^3(r)}{\left[1 + r^2\theta'^2(r)\right]^{3/2}}.$$

2. (a) On the basis of Fig. 1.3 the length of the thread unwound during the rotation by the angle ϕ is equal to the length $r_0\phi$ of the arc cut out by the angle from the circle. Thus, the vector directed to the point of the involute belonging to the parameter ϕ from the end of the vector $\mathbf{r}(\phi)$ has the length $r_0\phi$. On the basis of the figure the required expression for $\mathbf{R}(\phi)$, that is, the equation of the involute is

$$\mathbf{R}(\phi) = \mathbf{r}(\phi) + r_0\phi\mathbf{t}(\phi). \tag{2.116}$$

(b) The dot (scalar) product of the vectors

$$\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}\phi}(\phi) = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\phi}(\phi) + r_0\mathbf{t}(\phi) + r_0\phi\frac{\mathrm{d}\mathbf{t}}{\mathrm{d}\phi}(\phi)$$

and $\mathbf{t}(\phi)$ is

$$\begin{aligned}\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}\phi}(\phi)\cdot\mathbf{t}(\phi) &= \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\phi}(\phi)\cdot\mathbf{t}(\phi) + r_0\mathbf{t}(\phi)\cdot\mathbf{t}(\phi)\\ &\quad + r_0\phi\frac{\mathrm{d}\mathbf{t}}{\mathrm{d}\phi}(\phi)\cdot\mathbf{t}(\phi).\end{aligned} \tag{2.117}$$

Since

$$\mathbf{t}^2(\phi) = 1,$$

the last but one term on the right-hand side of Eqn (2.117) is r_0. Differentiating this last expression we obtain

$$2\mathbf{t}(\phi)\cdot\frac{\mathrm{d}\mathbf{t}}{\mathrm{d}\phi}(\phi) = 0,$$

that is the last term on the right-hand side of Eqn (2.117) vanishes. Taking into account the expressions

$$\mathbf{r}(\phi) = r_0(\cos\phi\mathbf{i} + \sin\phi\mathbf{j}), \tag{2.118}$$

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\phi}(\phi) = r_0(-\sin\phi\mathbf{i} + \cos\phi\mathbf{j}), \tag{2.119}$$

$$\left|\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\phi}(\phi)\right| = r_0$$

and

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\phi}(\phi) = -r_0\mathbf{t}(\phi) \tag{2.120}$$

we find that

$$\begin{aligned}\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}\phi}(\phi)\cdot\mathbf{t}(\phi) &= -r_0\mathbf{t}(\phi)\cdot\mathbf{t}(\phi) + r_0\\ &= -r_0 + r_0 = 0.\end{aligned}$$

The dot (scalar) product of $(\mathrm{d}\mathbf{R}/\mathrm{d}\phi)(\phi)$ and $\mathbf{t}(\phi)$ being zero, the two vectors are perpendicular to each other.

(c) With the help of Eqns (2.118) and (2.119) and the formula

$$\mathbf{t}(\phi) = -\frac{1}{r_0}\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\phi}(\phi)$$

obtained by the rearrangement of Eqn (2.120) it follows from Eqn (2.116) that

$$\mathbf{R}(\phi) = r_0(\cos\phi + \phi\sin\phi)\mathbf{i} + r_0(\sin\phi - \phi\cos\phi)\mathbf{j},$$

that is,

$$X(\phi) = r_0(\cos\phi + \phi\sin\phi),$$

$$Y(\phi) = r_0(\sin\phi - \phi\cos\phi).$$

From the last two formulas the distance d between the points $\mathbf{R}(\phi^*)$ and $\mathbf{R}(\phi^* + 2\pi)$ is

$$d = \sqrt{[X(\phi^* + 2\pi) - X(\phi^*)]^2 + [Y(\phi^* + 2\pi) - Y(\phi^*)]^2},$$

that is,

$$d = \sqrt{4r_0^2\pi^2\sin^2\phi^* + 4r_0^2\pi^2\cos^2\phi^*} = 2r_0\pi,$$

as it was expected on the basis of the previous definition of the involute.

3. (a) We shall apply Stokes' theorem,

$$\int_A \operatorname{curl}\mathbf{v}\mathrm{d}\mathbf{A} = \oint_C \mathbf{v}\,\mathrm{d}\mathbf{r},$$

in which $\mathbf{v}$ is a vector function, C is a closed curve and A is a surface whose boundary is C. Let T be a rectangle on which

$$B = \frac{\partial P}{\partial x} + \frac{\partial Q}{\partial y} \tag{2.121}$$

is everywhere positive or everywhere negative, and assume that T contains a closed trajectory C corresponding to a non-constant periodic solution of Eqn (1.104). Employing the equation

$$\operatorname{curl}\mathbf{v} = \operatorname{curl}(-Q\mathbf{i} + P\mathbf{j}) = \left(\frac{\partial P}{\partial x} + \frac{\partial Q}{\partial y}\right)\mathbf{k}$$

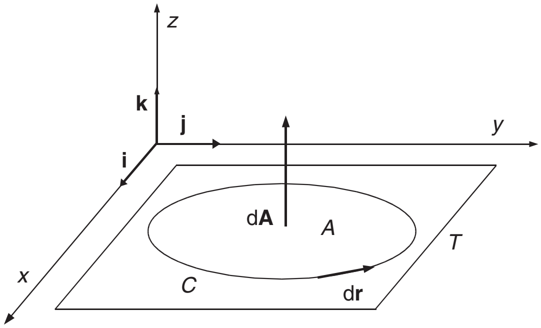


Figure 2.14 To Bendixson's criterion

concerning the vector function

$$\mathbf{v} = -Q\mathbf{i} + P\mathbf{j}$$

Stokes' theorem implies that

$$\int_A \left(\frac{\partial P}{\partial x} + \frac{\partial Q}{\partial y} \right) \mathrm{d}A = \oint_C (-Q\,\mathrm{d}x + P\,\mathrm{d}y),$$

where A is the planar domain bounded by the curve C (see Fig. 2.14). The integral on the left-hand side cannot be zero since the integrand is either positive or negative on the whole domain A lying in the inside of T. However, using Eqn (1.104) we obtain for the integral on the right-hand side that

$$\begin{aligned} \oint_C (-Q\,\mathrm{d}x + P\,\mathrm{d}y) &= \int_0^\lambda (-Q\dot{x} + P\dot{y})\,\mathrm{d}t \\ &= \int_0^\lambda (-QP + PQ)\,\mathrm{d}t = 0 \qquad (2.122) \end{aligned}$$

(λ is the period of the periodic solution corresponding to the closed trajectory C). The contradiction found proves Bendixson's criterion.

(b) Assume that there exists a closed trajectory C in the positive quadrant. Then Bendixson's criterion implies that

$$\begin{aligned} B(x,y) &= \frac{\partial P}{\partial x}(x,y) + \frac{\partial Q}{\partial y}(x,y) \\ &= a_2 + a_3 y + 2a_4 x + b_2 + b_3 x + 2b_4 y \qquad (2.123) \end{aligned}$$

is either identically zero or changes its sign on a rectangle T containing C. If the right-hand side of Eqn (2.123) is identically zero on T then the coefficients $\{a_2, a_3, a_4, b_2, b_3, b_4\}$ are all zero, and the right-hand sides in Eqn (1.104) contain non-negative functions. This latter fact excludes the existence of a non-constant periodic solution, which is a contradiction. If the right-hand side of Eqn (2.123) changes its sign on T, at least one of the coefficients $\{a_2, a_3, b_2, b_3\}$ must be positive. In the chemical terminology this latter means that at least one autocatalytic reaction – in which a product accelerates its own production – must take place in the system.

(c) Some calculation yields

$$B(x,y) = -\left(\frac{a_1}{x^2y} - \frac{a_4}{y} + \frac{a_5y}{x^2} + \frac{b_1}{xy^2} - \frac{b_4}{x} + \frac{b_5x}{y^2}\right).$$

It follows from the signs of the coefficients that either $B(x,y) < 0$ or $B(x,y) = 0$ in the whole positive quadrant. According to Bendixson's criterion, however, $B(x,y) < 0$ excludes the existence of a closed trajectory, so $B(x,y) = 0$ must be valid. This implies

$$a_1 = a_4 = a_5 = b_1 = b_4 = b_5 = 0,$$

which proves the assertion.

4. In spherical polar coordinates the volume element can be given as

$$\mathrm{d}V = r^2 \sin\theta \,\mathrm{d}r \,\mathrm{d}\phi \,\mathrm{d}\theta.$$

In the case of the orbital $2p_x$ we must determine the integral

$$I = \int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} r^4 e^{-(Zr/a_0)} \sin^3\theta \cos^2\phi \,\mathrm{d}r \,\mathrm{d}\phi \,\mathrm{d}\theta,$$

for which

$$I = \left(\int_0^{\pi} \sin^3\theta \,\mathrm{d}\theta\right)\left(\int_0^{2\pi} \cos^2\phi \,\mathrm{d}\phi\right)\left(\int_0^{\infty} r^4 e^{-(Zr/a_0)} \,\mathrm{d}r\right).$$

Employing

$$\int_0^{\pi} \sin^3\theta \,\mathrm{d}\theta = \left[-\cos\theta\left(\frac{\sin^2\theta + 2}{3}\right)\right]_0^{\pi} = \frac{4}{3},$$

$$\int_0^{2\pi} \cos^2\phi \,\mathrm{d}\phi = \left[\frac{1}{2}\phi + \frac{1}{4}\sin 2\phi\right]_0^{2\pi} = \pi$$

and

$$\int_0^\infty r^4 e^{-(Zr/a_0)}\,\mathrm{d}r = \frac{4!}{(Z/a_0)^5},$$

we obtain from the equation

$$N^2 I = 1 \tag{2.124}$$

that

$$N = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2}. \tag{2.125}$$

For the orbital $2p_y$

$$I = \left(\int_0^\pi \sin^3\theta\,\mathrm{d}\theta\right)\left(\int_0^{2\pi} \sin^2\phi\,\mathrm{d}\phi\right)\left(\int_0^\infty r^4 e^{-(Zr/a_0)}\,\mathrm{d}r\right),$$

in which we have already computed two integrals, and the one left is

$$\int_0^{2\pi} \sin^2\phi\,\mathrm{d}\phi = \left[\frac{1}{2}\phi - \frac{1}{4}\sin 2\phi\right]_0^{2\pi} = \pi.$$

Thus, Eqn (2.124) yields again Eqn (2.125). For the orbital $2p_z$ we have

$$I = \left(\int_0^\pi \cos^2\theta\sin\theta\,\mathrm{d}\theta\right)\left(\int_0^{2\pi} 1\,\mathrm{d}\phi\right)\left(\int_0^\infty r^4 e^{-(Zr/a_0)}\mathrm{d}r\right),$$

in which the integral with respect to r has already been determined, and the integrals with respect to the angles are as follows:

$$\int_0^\pi \cos^2\theta\sin\theta\,\mathrm{d}\theta\left[-\frac{\cos^3\theta}{3}\right]_0^\pi = \frac{2}{3}$$

and

$$\int_0^{2\pi} 1\,\mathrm{d}\phi = [\phi]_0^{2\pi} = 2\pi.$$

Eqn (2.124) results in again Eqn (2.125).

5. (a) Simple geometrical considerations yield

$$x = \frac{R}{2}\sqrt{(\xi_1^2 - 1)(1 - \xi_2^2)}\cos\xi_3, \tag{2.126}$$

$$y = \frac{R}{2}\sqrt{(\xi_1^2 - 1)(1 - \xi_2^2)}\sin\xi_3 \tag{2.127}$$

and

$$z = \frac{R}{2}\xi_1\xi_2. \tag{2.128}$$

(b) Differentiating the functions defined by Eqns (2.126)–(2.128), and employing the notation

$$T = \sqrt{(\xi_1^2 - 1)(1 - \xi_2^2)}$$

we obtain

$$\begin{aligned}
\frac{\partial x}{\partial \xi_1}(\xi_1, \xi_2, \xi_3) &= \frac{R}{2T}\xi_1(1 - \xi_2^2)\cos\xi_3,\\
\frac{\partial x}{\partial \xi_2}(\xi_1, \xi_2, \xi_3) &= -\frac{R}{2T}\xi_2(\xi_1^2 - 1)\cos\xi_3,\\
\frac{\partial x}{\partial \xi_3}(\xi_1, \xi_2, \xi_3) &= -\frac{R}{2}T\sin\xi_3
\end{aligned}$$

moreover,

$$\begin{aligned}
\frac{\partial y}{\partial \xi_1}(\xi_1, \xi_2, \xi_3) &= \frac{R}{2T}\xi_1(1 - \xi_2^2)\sin\xi_3,\\
\frac{\partial y}{\partial \xi_2}(\xi_1, \xi_2, \xi_3) &= -\frac{R}{2T}\xi_2(\xi_1^2 - 1)\sin\xi_3,\\
\frac{\partial y}{\partial \xi_3}(\xi_1, \xi_2, \xi_3) &= \frac{R}{2}T\cos\xi_3
\end{aligned}$$

and finally

$$\begin{aligned}
\frac{\partial z}{\partial \xi_1}(\xi_1, \xi_2, \xi_3) &= \frac{R}{2}\xi_2,\\
\frac{\partial z}{\partial \xi_2}(\xi_1, \xi_2, \xi_3) &= \frac{R}{2}\xi_1,\\
\frac{\partial z}{\partial \xi_3}(\xi_1, \xi_2, \xi_3) &= 0.
\end{aligned}$$

With these partial derivatives the quantities in Eqn (1.109) take the forms

$$h_1 = \sqrt{\frac{R^2\xi_1^2(1-\xi_2^2)^2}{4T^2} + \frac{R^2\xi_2^2}{4}},$$

$$h_2 = \sqrt{\frac{R^2\xi_2^2(\xi_1^2-1)^2}{4T^2} + \frac{R^2\xi_1^2}{4}}$$

and

$$h_3 = \frac{R}{2}T.$$

Using these values of h_1, h_2 and h_3 the combinations in Eqn (1.110) are as follows:

$$\begin{aligned} h_1h_2h_3 &= \frac{R^3}{8}(\xi_1^2-\xi_2^2), \\ \frac{h_2h_3}{h_1} &= \frac{R}{2}(\xi_1^2-1), \\ \frac{h_1h_3}{h_2} &= \frac{R}{2}(1-\xi_2^2) \end{aligned} \tag{2.129}$$

and finally

$$\frac{h_2h_1}{h_3} = \frac{R}{2}\frac{\xi_1^2-\xi_2^2}{(\xi_1^2-1)(1-\xi_2^2)}.$$

Inserting these formulas into Eqn (1.110) the final result will be

$$\begin{aligned} \Delta = \frac{4}{R^2(\xi_1^2-\xi_2^2)} \Bigg\{ &\frac{\partial}{\partial\xi_1}\left[(\xi_1^2-1)\frac{\partial}{\partial\xi_1}\right] \\ &+\frac{\partial}{\partial\xi_2}\left[(1-\xi_2^2)\frac{\partial}{\partial\xi_2}\right] \\ &+\frac{\xi_1^2-\xi_2^2}{(\xi_1^2-1)(1-\xi_2^2)}\frac{\partial^2}{\partial\xi_3^2}\Bigg\}. \end{aligned}$$

(c) Taking into account Eqns (1.111) and (2.129)

$$\mathrm{d}V = \frac{R^3}{8}(\xi_1^2-\xi_2^2)\,\mathrm{d}\xi_1\,\mathrm{d}\xi_2\,\mathrm{d}\xi_3,$$

so introducing the prolate spheroidal coordinates the integral

$$S = \int \frac{1}{\pi a_0^3} e^{-\frac{r_a + r_b}{a_0}} \mathrm{d}V$$

to be determined takes the form

$$S = \frac{R^3}{8\pi a_0^3} \int_0^{2\pi} \int_1^{\infty} \int_{-1}^{1} e^{-(R\xi_1/a_0)} (\xi_1^2 - \xi_2^2)\, \mathrm{d}\xi_2\, \mathrm{d}\xi_1\, \mathrm{d}\xi_3.$$

Integrating three times we obtain the final result

$$S = e^{-d}\left(\frac{d^2}{3} + d + 1\right); \quad d = \frac{R}{a_0}.$$

6. (a)

$$\Delta U = \int_G C_V\, \mathrm{d}T + \frac{\alpha}{V^2}\mathrm{d}V = \int_{T_1}^{T_2} \left(C_V \frac{\mathrm{d}T}{\mathrm{d}\xi} + \frac{\alpha}{V^2}\frac{\mathrm{d}V}{\mathrm{d}\xi}\right) \mathrm{d}\xi,$$

and since

$$\frac{\mathrm{d}T}{\mathrm{d}\xi} = 1; \quad \frac{\mathrm{d}V}{\mathrm{d}\xi} = \frac{V_2 - V_1}{T_2 - T_1},$$

it follows that

$$\Delta U = \int_{T_1}^{T_2} C_V\, \mathrm{d}\xi + \int_{T_1}^{T_2} \frac{\alpha}{\left(\frac{V_2 - V_1}{T_2 - T_1}\xi + \frac{V_1 T_2 - V_2 T_1}{T_2 - T_1}\right)^2} \frac{V_2 - V_1}{T_2 - T_1} \mathrm{d}\xi$$

(we also split the integral into two parts). Performing the integration

$$\Delta U = C_V\, [\xi]_{T_1}^{T_2} - \alpha \left[\frac{1}{\frac{V_2 - V_1}{T_2 - T_1}\xi + \frac{V_1 T_2 - V_2 T_1}{T_2 - T_1}}\right]_{T_1}^{T_2}$$

$$\Delta U = C_V(T_2 - T_1) - \alpha\left(\frac{1}{V_2} - \frac{1}{V_1}\right). \tag{2.130}$$

(b) In this case

$$\frac{\mathrm{d}T}{\mathrm{d}\xi}(\xi) = -\frac{T_1 T_2}{\xi^2}$$

and

$$\frac{\mathrm{d}V}{\mathrm{d}\xi} = -\frac{V_2 - V_1}{T_2 - T_1},$$

and we must integrate from $\xi = T_2$ to $\xi = T_1$ in order to proceed from the initial state towards the final state along the integration path. So

$$\Delta U = \int_{T_2}^{T_1} \left(C_V \frac{\mathrm{d}T}{\mathrm{d}\xi} + \frac{\alpha}{V^2} \frac{\mathrm{d}V}{\mathrm{d}\xi} \right) \mathrm{d}\xi$$

and

$$\Delta U = -C_V T_1 T_2 \int_{T_2}^{T_1} \frac{1}{\xi^2} \mathrm{d}\xi - \alpha \frac{V_2 - V_1}{T_2 - T_1} \int_{T_2}^{T_1} \frac{1}{\left(-\frac{V_2 - V_1}{T_2 - T_1}\xi + \frac{V_2 T_2 - V_1 T_1}{T_2 - T_1} \right)^2} \mathrm{d}\xi,$$

and performing the integration

$$\Delta U = C_V T_1 T_2 \left[\frac{1}{T} \right]_{T_2}^{T_1} - \alpha \left[\frac{1}{-\frac{V_2 - V_1}{T_2 - T_1}\xi + \frac{V_2 T_2 - V_1 T_1}{T_2 - T_1}} \right]_{T_2}^{T_1}.$$

This equation gives again Eqn (2.130). Since we obtained the same change ΔU along the two different curves, our results – and so Eqn (1.112) – are in accordance with the requirement concerning the internal energy.

7. (a) Since any amino acid molecule can be followed by any amino acid molecule, the number of the different peptide molecules is

$$\begin{matrix} & 1 & & 2 & \dots & K & \\ W = & N & \cdot & N \cdot & \dots \cdot & N & = N^K. \end{matrix}$$

The numerical results are collected in Table 2.6. The lower estimate is the full mass of $K \times W$ ^{12}C atoms in each case. For comparison we remark that the full mass of the Earth is 5.976×10^{24} kg.

(b) From $N - 1$ different amino acids we can create

$$(N - 1)^{K-L}$$

peptide molecules comprised of $K - L$ amino acid units. To obtain the desired molecules we insert different groups of L identical amino acid units of the specified type between the pairs of units of these peptide

Table 2.6 The number (W) and mass (m) of peptide molecules consisting of K units; the number of the amino acids is $N = 20$

K	W	$m >$(kg)
5	3.2×10^{6}	3.2×10^{-19}
20	$1.0485\ldots \times 10^{26}$	41.8
150	$1.4272\ldots \times 10^{195}$	4.2×10^{171}

molecules. There are $K - L + 1$ positions for the insertion of the different groups if we include also the two positions in front of and after a peptide molecule; the permutation of the L identical amino acids and $K - L$ identical separating lines gives the number of all the different insertion possibilities:

$$\frac{(K - L + L)!}{L!(K - L)!} = \binom{K}{L}.$$

Thus, the answer to the question is

$$W = \binom{K}{L}(N - 1)^{K-L}.$$

With the numerical data

$$W = \binom{150}{30}(20 - 1)^{150-30} = 9.0838\ldots \times 10^{184}.$$

The efficient synthesis of the different polypeptides is of extreme importance in chemistry and biology. The collection of synthetic methods using combinatorial considerations is usually called “combinatorial chemistry”. For the split-mix synthesis and historical overview see [92, 93].

8. We can place the particles onto the first, second and Kth energy level in $\binom{N}{N_1}$, $\binom{N - N_1}{N_2}$ and $\binom{N - N_1 - N_2 - \cdots - N_{K-1}}{N_K}$ ways, respectively. The total number of the possibilities (W_1) is the product of these numbers, that is,

$$W_1 = \binom{N}{N_1}\binom{N - N_1}{N_2}\cdots\binom{N - N_1 - N_2 - \ldots - N_{K-1}}{N_K},$$

which can be written as

$$W_1 = \frac{N!}{(N-N_1)!N_1!} \times \frac{(N-N_1)!}{(N-N_1-N_2)!N_2!}$$
$$\times \frac{(N-N_1-N_2-\cdots-N_{K-1})!}{(N-N_1-N_2-\cdots-N_K)!N_K!},$$

and so

$$W_1 = \frac{N!}{N_1!N_2!N_3!\ldots N_K!} = N!\prod_{i=1}^{K}\frac{1}{N_i!}.$$

If several states belong to the energy levels, there will be even more possibilities since the particles on a given energy level can be distributed among the different states in a number of ways. As any particle on the ith energy level can assume g_i states, the N_i particles can occupy these states in $g_i^{N_i}$ ways. Thus, the overall number of the possibilities becomes $W_2 = g_1^{N_1} g_2^{N_2} g_3^{N_3} \ldots g_i^{N_K} W_1$, that is,

$$W_2 = \frac{g_1^{N_1} g_2^{N_2} g_3^{N_3} \ldots g_k^{N_K} N!}{N_1!N_2!N_3!\ldots N_k!} = N!\prod_{i=1}^{K}\frac{g_i^{N_i}}{N_i!}.$$

9. We line up the N_i particles on the ith energy level and investigate the number of ways for the creation of groups of particles by $g_i - 1$ vertical separating lines. Each of the obtained g_i groups corresponds to an occupation of a state. For example, in the case of $N_i = 6$ and $g_i = 3$ several possibilites are as follows:

..|..|.. that is $2, 2, 2,$
|....|.. that is $0, 4, 2,$
....||.. that is $4, 0, 2.$

The number of all possible groups is equal to that of the possible permutations of $N_i + g_i - 1$ objects from which N_i and $g_i - 1$ objects are identical. Thus, the states on the ith energy level can be occupied in

$$W_i = \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

ways. The total number of the possibilities is

$$W = W_1 W_2 \ldots W_K = \prod_{i=1}^{K} W_i = \prod_{i=1}^{K} \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}.$$

10. First we give the number of the possible permutations of the N_i occupied states and the $g_i - N_i$ unoccupied states on the ith energy level (altogether we have g_i states here). The occupied states are indistinguishable and so are the unoccupied ones too. Thus, the states on the ith energy level can be occupied in

$$W_i = \frac{g_i!}{N_i!(g_i - N_i)!}$$

ways, and the total number of possibilities is obviously

$$W = W_1 W_2 \dots W_K = \prod_{i=1}^{K} W_i = \prod_{i=1}^{K} \frac{g_i!}{N_i!(g_i - N_i)!}.$$

11. (a) Suppose that in the chain leaning randomly a monomers point forwards and b monomers point backwards. In this case

$$a - b = n \quad \text{and} \quad a + b = N,$$

from which

$$a = \frac{N+n}{2} \quad \text{and} \quad b = \frac{N-n}{2}.$$

For a polymer molecule consisting of N monomers the total number of the possible monomer orientations is 2^N since each monomer can point in two directions. The number of the favourable cases – which takes the free end of the chain to the desired coordinate n – can be given as the number of the permutations of the $(N+n)/2$ “forwards” (F) and the $(N-n)/2$ “backwards” (B) positions. This number is

$$\frac{N!}{((N+n)/2)!((N-n)/2)!}.$$

For example, in the case of $N = 11$ and $n = 3$ several possibilities are as follows:

FFFFFFFHHHH
FFBBFFBBFFF
BFBFFFFFBFB.

Thus, the probability of the event that the free end of the chain consisting of N monomers is at the coordinate n is

$$p(n,N) = \frac{N!}{2^N((N+n)/2)!((N-n)/2)!}. \tag{2.131}$$

(b) Let the possible $|n| \le N$ values be $\pm n_0, \pm n_1, \ldots, \pm n_K$. Then the average of n is

$$\overline{n} = \sum_{i=0}^{K} \left[p(n_i, N) n_i + p(-n_i, N)(-n_i) \right].$$

Since Eqn (2.131) implies $p(n_i, N) = p(-n_i, N)$, it follows that

$$\overline{n} = 0.$$

At the same time the average of n^2 is

$$\begin{aligned}\overline{n^2} &= \sum_{i=0}^{K} \left[p(n_i, N) n_i^2 + p(-n_i, N)(-n_i)^2 \right] \\ &= 2 \sum_{i=0}^{K} p(n_i, N) n_i^2 > 0.\end{aligned}$$

Thus,

$$\sqrt{\overline{n^2}} \ne \overline{n}.$$

(c) Inserting $N = N_i$ into Eqn (2.131) and applying Stirling's formula to the factorials

$$P(n, N_i) = P_{\mathrm{a}}(n, N_i) e^{\theta_1/(4N_i) - \theta_2/(2N_i + 2n) - \theta_3/(2N_i - 2n)},$$

so

$$P(n, N_i) \le P_{\mathrm{a}}(n, N_i) e^{\theta_1/(4N_i)} \le P_{\mathrm{a}}(n, N_i) e^{1/(4N_i)}$$

and

$$\begin{aligned}P(n, N_i) &\ge P_{\mathrm{a}}(n, N_i) e^{-\theta_2/(2N_i + 2n) - \theta_3/(2N_i - 2n)} \\ &\ge P_{\mathrm{a}}(n, N_i) e^{-1/(2N_i + 2n) - 1/(2N_i - 2n)}.\end{aligned}$$

Thus,

$$e^{-1/(2N_i + 2n) - 1/(2N_i - 2n)} \le \frac{P(n, N_i)}{P_{\mathrm{a}}(n, N_i)} \le e^{1/(4N_i)},$$

from which

$$\lim_{i \to \infty} \frac{P(n, N_i)}{P_{\mathrm{a}}(n, N_i)} = 1.$$

Table 2.7 The values of $P(0, N_i)$ and $P_\mathrm{a}(0, N_i)$; for the calculation of $P(0, 100)$ the use of mathematical software is recommended

N_i	$P(0, N_i)$	$P_\mathrm{a}(0, N_i)$
6	$\frac{5}{16}$	0.3257...
10	$\frac{63}{256}$	0.2523...
100	0.0795...	0.0797...

The required probability values are given in Table 2.7. It can be seen that the free end of the chain returns to the origin with a probability that decreases as the number of the monomers increases. The convergence shown earlier is well reflected in the numerical results.

Appendix A Stoichiometry

The following considerations are mainly based on the works [26, 94–96].

A.1 THE FORMULA MATRIX

In the investigation of chemical reaction systems the formula matrix **A** plays an important role. Its *ki*th element gives the number of the *k*th atomic species in the *i*th substance. The size of the matrix **A** is $M \times N$, where M is the number of the atomic species and N the number of the substances in the reaction system. If there are ions in the reaction system, we also regard the electric charge (q) as an atomic species and write the charges of the substances including their signs in the last row of the formula matrix (for neutral particles write 0).

As an example, consider the simple system H_2SO_4–HSO_4^-–SO_4^{2-}–H^+ whose 4×4 formula matrix is

$$\begin{array}{ccccc} & \mathrm{H_2SO_4} & \mathrm{HSO_4^-} & \mathrm{SO_4^{2-}} & \mathrm{H^+} \\ \mathrm{H} & 2 & 1 & 0 & 1 \\ \mathrm{S} & 1 & 1 & 1 & 0 \\ \mathrm{O} & 4 & 4 & 4 & 0 \\ q & 0 & -1 & -2 & 1 \end{array} \tag{A.1}$$

or simply

$$\mathbf{A} = \begin{pmatrix} 2 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \\ 4 & 4 & 4 & 0 \\ 0 & -1 & -2 & 1 \end{pmatrix}.$$

If we change the numbering of the atomic species or the substances, the formula matrix may change but its chemical meaning remains the same.

The law of the conservation of atomic species is valid for any closed chemical system. The mathematical formulation of this law is

$$\sum_{i=1}^{N} a_{ki} \Delta n_i = 0; \qquad k = 1, 2, \ldots, M, \tag{A.2}$$

where $\Delta n_1, \Delta n_2, \ldots, \Delta n_N$ are the changes in the amounts of matter of the substances, a_{ki} is the kith element of the formula matrix **A** (we recall that this element gives the number of the kth atomic species in the ith substance), N the number of the substances and M the number of the atomic species in the system.

Mathematically, Eqn (A.2) has a non-zero solution $(\Delta n_1, \Delta n_2, \ldots, \Delta n_N)$ if and only if

$$\rho < N, \tag{A.3}$$

where ρ is the rank of matrix **A**. In the following we shall always assume the validity of Eqn (A.3).

A.2 REACTIONS

A vector $(\nu_1,\ \nu_2, \ldots, \nu_N)^{\mathrm{T}}$ whose components fulfil the system

$$\sum_{i=1}^{N} a_{ki} \nu_i = 0; \qquad k = 1, 2, \ldots, M \tag{A.4}$$

("balancing") is called a reaction of the chemical reaction system. A reaction can be written in the form

$$\sum_{i=1}^{N} \nu_i B_i = 0, \tag{A.5}$$

where B_i is the symbol of the ith reacting substance.

Eqn (A.4) also has a non-zero solution $(\nu_1, \nu_2,\ \ldots, \nu_N)$ if and only if Eqn (A.3) is valid. Thus, Eqn (A.3) is also the necessary and sufficient condition of the creation of a chemical reaction.

According to the theorems of linear algebra, Eqn (A.4) has $N - \rho$ linearly independent solutions, which means that a chemical system has $N - \rho$ linearly independent reaction vectors.

Since $a_{ki} \geq 0$ except for the a_{ki} coefficients corresponding to the electric charge, some of the coefficients ν_i satisfying Eqn (A.4) must be negative. For the sake of the "traditional" notation the *i*th substance in a given reaction is called a reactant if $\nu_i < 0$ and a product if $\nu_i > 0$. With this distinction the reactants can be grouped on the left-hand side of the equality sign and the products on the right-hand side:

$$\sum_{i=1;\nu_i<0}^{N} |\nu_i|\, \mathrm{B}_i = \sum_{i=1;\nu_i>0}^{N} \nu_i \mathrm{B}_i.$$

Not necessarily one set of independent reactions can be assigned to a given formula matrix, that is, to a given chemical system by the previous method, and the possible sets of reactions – beyond the conservation of atomic species and electric charge – do not necessarily correspond to real molecular events. It is true, however, that any reaction expressing a real molecular event obeys Eqn (A.4).

As an example we take the system H_2SO_4–HSO_4^-–SO_4^{2-}–H^+ whose formula matrix was already given previously. Here the number of the linearly independent reactions is $N - \rho = 4 - 2 = 2$. The stoichiometric coefficients of the reactions

$$\nu_1 H_2SO_4 + \nu_2 HSO_4^- + \nu_3 SO_4^{2-} + \nu_4 H^+ = 0$$

must obey – on the basis of Eqns (A.1) and (A.4) – the following equations:

$$\begin{aligned} 2\nu_1 + \nu_2 + \nu_4 &= 0, \\ \nu_1 + \nu_2 + \nu_3 &= 0, \\ 4\nu_1 + 4\nu_2 + 4\nu_3 &= 0, \\ -\nu_2 - 2\nu_3 + \nu_4 &= 0. \end{aligned} \tag{A.6}$$

It is easy to see that the reactions

$$-H_2SO_4 + HSO_4^- + H^+ = 0 \tag{A.7}$$

and

$$-HSO_4^- + SO_4^{2-} + H^+ = 0 \tag{A.8}$$

corresponding to

$$(\nu_1, \nu_2, \nu_3, \nu_4)^{\mathrm{T}} = (-1, 1, 0, 1)^{\mathrm{T}}$$

and

$$(\nu_1, \nu_2, \nu_3, \nu_4)^{\mathrm{T}} = (0, -1, 1, 1)^{\mathrm{T}}$$

satisfy Eqn (A.6). However, this latter is valid for the reactions

$$-H_2SO_4 + SO_4^{2-} + 2H^+ = 0 \tag{A.9}$$

or

$$-2H_2SO_4 + HSO_4^- + SO_4^{2-} + 3H^+ = 0 \tag{A.10}$$

as well. Some linearly independent reaction pairs are (A.7) and (A.8); (A.8) and (A.9); (A.9) and (A.10).

A.3 THE STOICHIOMETRIC MATRIX

The stoichiometric matrix is used for the concise description of the stoichiometry of a given reaction system. If the system contains N substances and R reactions, the stoichiometric matrix consists of N rows and R columns. The ijth element of this matrix, ν_{ij}, gives the stoichiometric coefficient of the ith substance in the jth reaction written as Eqn (A.5).

Of course, we can assign a stoichiometric matrix to a given set of "traditional" reactions as well. In this case we set $\nu_{ij} < 0$ for the reactants, $\nu_{ij} > 0$ for the products and $\nu_{ij} = 0$ for the substances that do not participate in the given reaction.

Using the indicated numbering the 4 × 2 stoichiometric matrix of the reaction system

$$\begin{aligned} H_2SO_4(1) &= H^+(4) + HSO_4^-(2) \quad [1] \\ HSO_4^- &= H^+ + SO_4^{2-}(3) \qquad [2] \end{aligned}$$

containing proper chemical formulas is

$$\begin{array}{ccc} & [1] & [2] \\ (1) & -1 & 0 \\ (2) & 1 & -1 \\ (3) & 0 & 1 \\ (4) & 1 & 1 \end{array},$$

that is,

$$\mathbf{S} = \begin{pmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \\ 1 & 1 \end{pmatrix}.$$

However, we do not need proper chemical formulas for the formal construction of a stoichiometric matrix. An example of this is the reaction system

$$\begin{aligned} B_1 + 2B_2 &= B_3 && [1] \\ B_3 + B_4 &= B_5 && [2] \\ 3B_1 + 2B_5 &= B_2 + 2B_6. && [3] \end{aligned}$$

According to the previous considerations the 6×3 stoichiometric matrix of this system is

$$\begin{array}{cccc} & [1] & [2] & [3] \\ B_1 & -1 & 0 & -3 \\ B_2 & -2 & 0 & 1 \\ B_3 & 1 & -1 & 0 \\ B_4 & 0 & -1 & 0 \\ B_5 & 0 & 1 & -2 \\ B_6 & 0 & 0 & 2 \end{array},$$

that is,

$$\mathbf{S} = \begin{pmatrix} -1 & 0 & -3 \\ -2 & 0 & 1 \\ 1 & -1 & 0 \\ 0 & -1 & 0 \\ 0 & 1 & -2 \\ 0 & 0 & 2 \end{pmatrix}.$$

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Appendix B Notation

B.1 CHEMISTRY

Because of the diversity of the chemical notations many chemical symbols are explained in the problems where they occur. Here the most general quantities have been collected. The (rounded) numerical values were taken from [97] and [98].

$a_0 = 5.2918 \times 10^{-11}\,\mathrm{m}$	Bohr radius
$c = 2.9979 \times 10^{8}\,\mathrm{m\,s^{-1}}$	the speed of light in vacuum
$h = 6.6261 \times 10^{-34}\,\mathrm{Js}$	Planck constant
$\hbar = \frac{h}{2\pi} = 1.0546 \times 10^{-34}\,\mathrm{Js}$	h cross
$k = 1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}}$	Boltzmann constant
$K_\mathrm{w} = 1.0 \times 10^{-14}$	autoprotolysis constant of water at 25°C
$R = 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}$	universal gas constant
n	amount of substance
p	pressure
V	volume
T	thermodynamical temperature
b	molality
c	amount concentration or molarity
$[\mathrm{A}]$	the amount concentration of the substance A
$[\mathrm{A}]_0$	initial concentration
$b^{\ominus} = 1\,\mathrm{mol\,kg^{-1}}$	the unit of molality
$c^{\ominus} = 1\,\mathrm{mol\,dm^{-3}}$	the unit of amount concentration
t	time

B.2 MATHEMATICS

$a \in A$	a belongs to the set A
$A \subset B$	A is a subset of B
(a, b)	an open interval with the endpoints $a < b$
$[a, b]$	a closed interval with the endpoints $a < b$
$[a, b),\ (a, b]$	half-closed intervals with the endpoints $a < b$
$\mathbb{R}^n$	the n-dimensional Euclidean space
$\mathbb{R}^n_+$	the set of points in $\mathbb{R}^n$ having positive coordinates
$\mathbb{R}^1, \mathbb{R}$	the one-dimensional Euclidean space
$(x, y), (x, y, z), (c_1, c_2, \ldots, c_n)$	points or vector functions in $\mathbb{R}^2$, $\mathbb{R}^3$ and $\mathbb{R}^n$, respectively
f	a function
$f : (a, b) \to \mathbb{R}$	a univariate function mapping from (a, b) to $\mathbb{R}$
$f(x)$	the value of the univariate function f at the variable value x
$f(x, y)$	the value of the bivariate function f at the point (x, y)
$f(x, y, z)$	the value of the trivariate function f at the point (x, y, z)
$f(c_1, c_2, \ldots, c_n)$	the value of the multivariate function f at the point $(c_1, c_2, \ldots, c_n)$
$\frac{df}{dx}(x),\ f'(x),\ \dot{f}(x)$	the first derivative of the univariate function f at the point x
$\frac{d^2f}{dx^2}(x),\ f''(x),\ \ddot{f}(x)$	the second derivative of the univariate function f at the point x
$\frac{d^nf}{dx^n}(x),\ f^{(n)}(x)$	the nth derivative of the univariate function f at the value x

$\frac{\partial f}{\partial x}(x, y, z)$, $f'_x(x, y, z)$	the first partial derivative of the trivariate function f with respect to the variable x at the point (x, y, z)
$\frac{\partial f}{\partial x_i}(x_1, x_2, \ldots, x_n), f'_{x_i}(x_1, x_2, \ldots, x_n),$ $\partial_i f(x_1, x_2, \ldots, x_n)$	the first partial derivative of the multivariate function f with respect to x_i at the point $(x_1, x_2, \ldots, x_n)$
$\frac{\partial^2 f}{\partial x^2}(x, y, z), f''_{xx}(x, y, z)$	the second partial derivative of the trivariate function f with respect to x at the point (x, y, z)
$\frac{\partial^2 f}{\partial y \partial x}(x, y), f''_{xy}(x, y)$	a mixed partial derivative of the bivariate function f at the point (x, y) (first we differentiate with respect to x and then to y)
$\int f(x)\,dx, \int f\,dx$	the indefinite integral of the univariate function f
$\int_a^b f(x)\,dx, \int_a^b f\,dx$	the definite integral of the univariate function f over the interval $[a, b]$
$\lim_{x \to a} f(x) = b, f(x) \to b$ if $x \to a$	the limit of the univariate function f is b when x tends to a
$\mathbf{a}$, $\mathbf{A}$, $\mathbf{b}$, $\mathbf{B}$	vectors or matrices
a_i, b_{ij}	the ith element of a row or column matrix; the ijth element of a matrix
$\mathbf{i}, \mathbf{j}, \mathbf{k}$	orthogonal unit vectors
$\mathbf{a} \cdot \mathbf{b}, (\mathbf{a}, \mathbf{b})$	the dot product (scalar product) of the vectors $\mathbf{a}$ and $\mathbf{b}$
$\mathbf{a} \times \mathbf{b}, [\mathbf{a}, \mathbf{b}]$	the cross product (vectorial product) of the vectors $\mathbf{a}$ and $\mathbf{b}$

$\frac{d\mathbf{r}}{dt}, \dot{\mathbf{r}}$	the first derivative of the vector function $\mathbf{r}$ with respect to t
$\frac{d\mathbf{r}}{dt}(t), \dot{\mathbf{r}}(t)$	the value of the function $\frac{d\mathbf{r}}{dt}$ or $\dot{\mathbf{r}}$ at the point t
δ_{ij}	Kronecker delta, $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$
$\begin{vmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{vmatrix}$; $\det \mathbf{A}$	a determinant; the determinant of the matrix $\mathbf{A}$
$\mathbf{A}^{-1}$	the inverse of the matrix $\mathbf{A}$
$\mathbf{A}^{\mathrm{T}}$	the transpose of the matrix $\mathbf{A}$
$\int_A \mathbf{v}\, \mathrm{d}\mathbf{A}$	the integral of the vector function $\mathbf{v}$ over the surface A
$\int_C \mathbf{v}\, \mathrm{d}\mathbf{s}$	the integral of the vector function $\mathbf{v}$ on the curve C
$n!$	n factorial
$\binom{n}{k}$	binomial coefficient, "n choose k"
$< c >, \bar{c}$	the average value of c

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