Solutions Manual for Mathematics for Physical Chemistry

Solutions Manual for Mathematics for Physical Chemistry

Fourth Edition

Robert G. Mortimer
Professor Emeritus
Rhodes College
Memphis, Tennessee

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Preface

This book provides solutions to nearly of the exercises and problems in *Mathematics for Physical Chemistry*, fourth edition, by Robert G. Mortimer. This edition is a revision of a third edition published by Elsevier/Academic Press in 2005. Some of exercises and problems are carried over from earlier editions, but some have been modified, and some new ones have been added. I am pleased to acknowledge the cooperation and help of Linda Versteeg-Buschman, Beth Campbell, Jill Cetel, and their collaborators at Elsevier. It is also a pleasure to acknowledge the assistance of all those who helped with all editions of the book for which this is the solutions manual, and especially to thank my wife, Ann, for her patience, love, and forbearance.

There are certain errors in the solutions in this manual, and I would appreciate learning of them through the publisher.

Robert G. Mortimer

Chapter 1

Problem Solving and Numerical Mathematics

EXERCISES

Exercise 1.1. Take a few fractions, such as $\frac{2}{3}, \frac{4}{9}$ or $\frac{3}{7}$ and represent them as decimal numbers, finding either all of the nonzero digits or the repeating pattern of digits.

$$\begin{aligned}\frac{2}{3} &= 0.66666666\cdots \\ \frac{4}{9} &= 0.4444444\cdots \\ \frac{3}{7} &= 0.428571428571\cdots\end{aligned}$$

Exercise 1.2. Express the following in terms of SI base units. The electron volt (eV), a unit of energy, equals 1.6022×10^{-18} J.

a. $(13.6 \text{ eV})\left(\dfrac{1.6022 \times 10^{-19} \text{ J}}{1 \text{ eV}}\right) = 2.17896 \times 10^{-19} \text{ J}$
$\approx 2.18 \times 10^{-18}$ J

b. $(24.17 \text{ mi})\left(\dfrac{5280 \text{ ft}}{1 \text{ mi}}\right)\left(\dfrac{12 \text{ in}}{1 \text{ ft}}\right)\left(\dfrac{0.0254m}{1 \text{ in}}\right)$
$= 3.890 \times 10^4$ m

c. $(55 \text{ mi h}^{-1})\left(\dfrac{5280 \text{ ft}}{1 \text{ mi}}\right)\left(\dfrac{12 \text{ in}}{1 \text{ ft}}\right)\left(\dfrac{0.0254 \text{ m}}{1 \text{ in}}\right)$
$\left(\dfrac{1 \text{ h}}{3600 \text{ s}}\right) = 24.59 \text{ m s}^{-1} \approx 25 \text{ m s}^{-1}$

d. $(7.53 \text{ nm ps}^{-1})\left(\dfrac{1 \text{ m}}{10^9 \text{ nm}}\right)\left(\dfrac{10^{12} \text{ ps}}{1 \text{ s}}\right)$
$= 7.53 \times 10^3 \text{ m s}^{-1}$

Exercise 1.3. Convert the following numbers to scientific notation:

a. $0.00000234 = 2{,}34 \times 10^{-6}$
b. $32.150 = 3.2150 \times 10^1$

Exercise 1.4. Round the following numbers to three significant digits

a. $123456789123 \approx 123{,}000{,}000{,}000$
b. $46.45 \approx 46.4$

Exercise 1.5. Find the pressure P of a gas obeying the ideal gas equation

$$PV = nRT$$

if the volume V is 0.200 m^3, the temperature T is 298.15 K and the amount of gas n is 1.000 mol. Take the smallest and largest value of each variable and verify your number of significant digits. Note that since you are dividing by V the smallest value of the quotient will correspond to the largest value of V.

$$\begin{aligned}P &= \frac{nRT}{V} \\ &= \frac{(1.000 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{0.200 \text{ m}^3} \\ &= 12395 \text{ J m}^{-3} = 12395 \text{ N m}^{-2} \approx 1.24 \times 10^4 \text{ Pa} \\ P_{\text{max}} &= \frac{nRT}{V} \\ &= \frac{(1.0005 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.155 \text{ K})}{0.1995 \text{ m}^3} \\ &= 1.243 \times 10^4 \text{ Pa} \\ P_{\text{min}} &= \frac{nRT}{V} \\ &= \frac{(0.9995 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.145 \text{ K})}{0.2005 \text{ m}^3} \\ &= 1.236 \times 10^4 \text{ Pa}\end{aligned}$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00025-2

Exercise 1.6. Calculate the following to the proper numbers of significant digits.

a. $17.13 + 14.6751 + 3.123 + 7.654 - 8.123 = 34.359 \approx 34.36$

b. $\ln(0.000123)$

$$\ln(0.0001235) = -8.99927$$
$$\ln(0.0001225) = -9.00740$$

The answer should have three significant digits:

$$\ln(0.000123) = -9.00$$

PROBLEMS

1. Find the number of inches in 1.000 meter.

$$(1.000\ \mathrm{m})\left(\frac{1\ \mathrm{in}}{0.0254\ \mathrm{m}}\right) = 39.37\ \mathrm{in}$$

2. Find the number of meters in 1.000 mile and the number of miles in 1.000 km, using the definition of the inch.

$$(1.000\ \mathrm{mi})\left(\frac{5280\ \mathrm{ft}}{1\ \mathrm{mi}}\right)\left(\frac{12\ \mathrm{in}}{1\ \mathrm{ft}}\right)\left(\frac{0.0254\ \mathrm{m}}{1\ \mathrm{in}}\right) = 1609\ \mathrm{m}$$

$$(1.000\ \mathrm{km})\left(\frac{1000\ \mathrm{m}}{1\ \mathrm{km}}\right)\left(\frac{1\ \mathrm{in}}{0.0254\ \mathrm{m}}\right)\left(\frac{1\ \mathrm{ft}}{12\ \mathrm{in}}\right) \times \left(\frac{1\ \mathrm{mi}}{5280\ \mathrm{ft}}\right) = 0.6214$$

3. Find the speed of light in miles per second.

$$(299792458\ \mathrm{m\ s^{-1}})\left(\frac{1\ \mathrm{in}}{0.0254\ \mathrm{m}}\right)\left(\frac{1\ \mathrm{ft}}{12\ \mathrm{in}}\right) \times \left(\frac{1\ \mathrm{mi}}{5280\ \mathrm{ft}}\right) = 186282.397\ \mathrm{mi\ s^{-1}}$$

4. Find the speed of light in miles per hour.

$$(299792458\ \mathrm{m\ s^{-1}})\left(\frac{1\ \mathrm{in}}{0.0254\ \mathrm{m}}\right)\left(\frac{1\ \mathrm{ft}}{12\ \mathrm{in}}\right) \times \left(\frac{1\ \mathrm{mi}}{5280\ \mathrm{ft}}\right)\left(\frac{3600\ \mathrm{s}}{1\ \mathrm{h}}\right) = 670616629\ \mathrm{mi\ h^{-1}}$$

5. A furlong is exactly one-eighth of a mile and a fortnight is exactly 2 weeks. Find the speed of light in furlongs per fortnight, using the correct number of significant digits.

$$(299792458\ \mathrm{m\ s^{-1}})\left(\frac{1\ \mathrm{in}}{0.0254\ \mathrm{m}}\right)\left(\frac{1\ \mathrm{ft}}{12\ \mathrm{in}}\right) \times \left(\frac{1\ \mathrm{mi}}{5280\ \mathrm{ft}}\right)\left(\frac{8\ \mathrm{furlongs}}{1\ \mathrm{mi}}\right) \times \left(\frac{3600\ \mathrm{s}}{1\ \mathrm{h}}\right)\left(\frac{24\ \mathrm{h}}{1\ \mathrm{d}}\right)\left(\frac{14\ \mathrm{d}}{1\ \mathrm{fortnight}}\right) = 1.80261750 \times 10^{12}\ \mathrm{furlongs\ fortnight^{-1}}$$

6. The distance by road from Memphis, Tennessee to Nashville, Tennessee is 206 miles. Express this distance in meters and in kilometers.

$$(206\ \mathrm{mi})\left(\frac{5380\ \mathrm{ft}}{1\ \mathrm{mi}}\right)\left(\frac{12\ \mathrm{in}}{1\ \mathrm{ft}}\right)\left(\frac{0.0254\ \mathrm{m}}{1\ \mathrm{in}}\right) = 3.32 \times 10^{5}\ \mathrm{m} = 332\ \mathrm{km}$$

7. A U. S. gallon is defined as 231.00 cubic inches.

a. Find the number of liters in 1.000 gallon.

$$(1\ \mathrm{gal})\left(\frac{231.00\ \mathrm{in^3}}{1\ \mathrm{gal}}\right)\left(\frac{0.0254\ \mathrm{m}}{1\ \mathrm{in}}\right)^3\left(\frac{1000\ \mathrm{l}}{1\ \mathrm{m^3}}\right) = 3.785\ \mathrm{l}$$

b. The volume of 1.0000 mol of an ideal gas at 0.00 °C (273.15 K) and 1.000 atm is 22.414 liters. Express this volume in gallons and in cubic feet.

$$(22.414\ \mathrm{l})\left(\frac{1\ \mathrm{m^3}}{1000\ \mathrm{l}}\right)\left(\frac{1\ \mathrm{in}}{0.0254\ \mathrm{m^3}}\right)^3 \times \left(\frac{1\ \mathrm{gal}}{231.00\ \mathrm{in^3}}\right) = 5.9212\ \mathrm{gal}$$

$$(22.414\ \mathrm{l})\left(\frac{1\ \mathrm{m^3}}{1000\ \mathrm{l}}\right)\left(\frac{1\ \mathrm{in}}{0.0254\ \mathrm{m^3}}\right)^3 \times \left(\frac{1\ \mathrm{ft}}{12\ \mathrm{in}}\right)^3 = 0.79154\ \mathrm{ft^3}$$

8. In the USA, footraces were once measured in yards and at one time, a time of 10.00 seconds for this distance was thought to be unattainable. The best runners now run 100 m in 10 seconds or less. Express 100.0 m in yards. If a runner runs 100.0 m in 10.00 s, find his time for 100 yards, assuming a constant speed.

$$(100.0\ \mathrm{m})\left(\frac{1\ \mathrm{in}}{0.0254\ \mathrm{m}}\right)\left(\frac{1\ \mathrm{yd}}{36\ \mathrm{in}}\right) = 109.4\ \mathrm{m}$$

$$(10.00\ \mathrm{s})\left(\frac{100.0\ \mathrm{yd}}{109.4\ \mathrm{m}}\right) = 9.144\ \mathrm{s}$$

9. Find the average length of a century in seconds and in minutes. Use the rule that a year ending in 00 is not a leap year unless the year is divisible by 400, in which case it is a leap year. Therefore, in four centuries there will be 97 leap years. Find the number of minutes in a microcentury.

Number of days in 400 years

$$= (365\ \text{d})(400\ \text{y}) + 97\ \text{d} = 146097\ \text{d}$$

Average number of days in a century

$$= \frac{146097\ \text{d}}{4} = 36524.25\ \text{d}$$

$$1\ \text{century} = (36524.25\ \text{d})\left(\frac{24\ \text{h}}{1\ \text{d}}\right)\left(\frac{60\ \text{min}}{1\ \text{h}}\right)$$

$$= 5.259492 \times 10^{7}\ \text{min}$$

$$(5.259492 \times 10^{7}\ \text{min})\left(\frac{1\ \text{century}}{1 \times 10^{6}\ \text{microcenturies}}\right)$$

$$= 52.59492\ \text{min}$$

$$(52.59492\ \text{min})\left(\frac{60\ \text{s}}{1\ \text{min}}\right) = 3155.695\ \text{s}$$

10. A light year is the distance traveled by light in one year.

a. Express this distance in meters and in kilometers. Use the average length of a year as described in the previous problem. How many significant digits can be given?

$$(299792458\ \text{m s}^{-1})\left(\frac{60\ \text{s}}{1\ \text{min}}\right)$$

$$\times (5.259492 \times 10^{5}\ \text{min})$$

$$= (9.46055060 \times 10^{15}\ \text{m})$$

$$(9.46055060 \times 10^{15}\ \text{m})\left(\frac{1\ \text{km}}{1000\ \text{m}}\right)$$

$$= 9.4605506 \times 10^{12}\ \text{km}$$

$$\approx 9.460551 \times 10^{12}\ \text{km}$$

Since the number of significant digits in the number of days in an average century is seven, we round to seven significant digits.

b. Express a light year in miles.

$$(9.460551 \times 10^{15}\ \text{m})\left(\frac{1\ \text{in}}{0.0254\ \text{m}}\right)\left(\frac{1\ \text{ft}}{12\ \text{in}}\right)$$

$$\times \left(\frac{1\ \text{mi}}{5280\ \text{ft}}\right) = 5.878514 \times 10^{12}\ \text{mi}$$

11. The Rankine temperature scale is defined so that the Rankine degree is the same size as the Fahrenheit degree, and absolute zero is 0 °R, the same as 0 K.

a. Find the Rankine temperature at 0.00 °C.

$$0.00\ °\text{C} \leftrightarrow (273.15\ \text{K})\left(\frac{9\ °\text{F}}{5\ \text{K}}\right) = 491.67\ °\text{R}$$

b. Find the Rankine temperature at 0.00 °F.

$$273.15\ \text{K} - 18.00\ \text{K} = 255.15\ \text{K}$$

$$(255.15\ \text{K})\left(\frac{9\ °\text{F}}{5\ \text{K}}\right) = 459.27\ °\text{R}$$

12. The volume of a sphere is given by

$$V = \frac{4}{3}\pi r^{3}$$

where V is the volume and r is the radius. If a certain sphere has a radius given as 0.005250 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the sphere might have with the given information and check your first answer for the volume.

$$V = \frac{4}{3}\pi r^{3} = V = \frac{4}{3}\pi (0.005250\ \text{m})^{3}$$

$$= 6.061 \times 10^{-7}\ \text{m}^{3}$$

$$V_{\text{min}} = \frac{4}{3}\pi (0.005245\ \text{m})^{3} = 6.044 \times 10^{-7}\ \text{m}^{3}$$

$$V_{\text{max}} = \frac{4}{3}\pi (0.005255\ \text{m})^{3} = 6.079 \times 10^{-7}\ \text{m}^{3}$$

$$V = 6.06 \times 10^{-7}\ \text{m}^{3}$$

The rule of thumb gives four significant digits, but the calculation shows that only three significant digits can be specified and that the last digit can be wrong by one.

13. The volume of a right circular cylinder is given by

$$V = \pi r^{2} h,$$

where r is the radius and h is the height. If a right circular cylinder has a radius given as 0.134 m and a height given as 0.318 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the cylinder might have with the given information and check your first answer for the volume.

$$V = \pi (0.134\ \text{m})^{2}(0.318\ \text{m}) = 0.0179\ \text{m}^{3}$$

$$V_{\text{min}} = \pi (0.1335\ \text{m})^{2}(0.3175\ \text{m}) = 0.01778\ \text{m}^{3}$$

$$V_{\text{max}} = \pi (0.1345\ \text{m})^{2}(0.3185\ \text{m}) = 0.0181\ \text{m}^{3}$$

14. The value of an angle is given as 31°. Find the measure of the angle in radians. Find the smallest and largest values that its sine and cosine might have and specify the sine and cosine to the appropriate number of digits.

$$(31°)\left(\frac{2\pi \text{ rad}}{360°}\right) = 0.54 \text{ rad}$$
$$\sin(30.5°) = 0.5075$$
$$\sin(31.5°) = 0.5225$$
$$\sin(31°) = 0.51$$
$$\cos(30.5°) = 0.86163$$
$$\cos(31.5°) = 0.85264$$
$$\cos(31°) = 0.86$$

15. Some elementary chemistry textbooks give the value of R, the ideal gas constant, as 0.0821 l atm K^{-1} mol^{-1}.

a. Using the SI value, 8.3145 J K^{-1} mol^{-1}, obtain the value in l atm K^{-1} mol^{-1} to five significant digits.

$$(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})\left(\frac{1 \text{ Pa m}^3}{1 \text{ J}}\right)\left(\frac{1 \text{ atm}}{101325 \text{ Pa}}\right) \times \left(\frac{1000 \text{ l}}{1 \text{ m}^3}\right) = 0.082058 \text{ l atm K}^{-1} \text{ mol}^{-1}$$

b. Calculate the pressure in atmospheres and in N m^{-2} (Pa) of a sample of an ideal gas with $n = 0.13678$ mol, $V = 10.000$ l and $T = 298.15$ K.

$$P = \frac{nRT}{V} = \frac{(0.13678 \text{ mol})(0.082058 \text{ l atm K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{1.000 \text{ l}} = 0.33464 \text{ atm}$$

$$P = \frac{nRT}{V} = \frac{(0.13678 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{10.000 \times 10^{-3} \text{ m}^3} = 3.3907 \times 10^4 \text{ J m}^{-3} = 3.3907 \times 10^4 \text{ N m}^{-2} = 3.3907 \times 10^4 \text{ Pa}$$

16. The van der Waals equation of state gives better accuracy than the ideal gas equation of state. It is

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

where a and b are parameters that have different values for different gases and where $V_m = V/n$, the molar volume. For carbon dioxide, $a = 0.3640$ Pa m^6 mol^{-2}, $b = 4.267 \times 10^{-5}$ m^3 mol^{-1}. Calculate the pressure of carbon dioxide in pascals, assuming that $n = 0.13678$ mol, $V = 10.00$ l, and $T = 298.15$ K. Convert your answer to atmospheres and torr.

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1} - 4.267 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}} - \frac{0.3640 \text{ Pa m}^6 \text{ mol}^{-2}}{(7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1})^2}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1} - 4.267 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}} - \frac{0.3640 \text{ Pa m}^6 \text{ mol}^{-2}}{(7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1})^2}$$
$$= 3.3927 \times 10^4 \text{ J m}^{-3} - 68.1 \text{ Pa}$$
$$= 3.3927 \times 10^4 \text{ Pa} - 68.1 \text{ Pa} = 3.386 \text{ Pa}$$
$$(3.3859 \text{ Pa})\left(\frac{1 \text{ atm}}{101325 \text{ Pa}}\right) = 0.33416 \text{ atm}$$

The prediction of the ideal gas equation is

$$P = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}} = 3.3907 \times 10^4 \text{ J m}^{-3} = 3.3907 \times 10^4 \text{ Pa}$$

17. The specific heat capacity (specific heat) of a substance is crudely defined as the amount of heat required to raise the temperature of unit mass of the substance by 1 degree Celsius (1 °C). The specific heat capacity of water is 4.18 J $°C^{-1}$ g^{-1}. Find the rise in temperature if 100.0 J of heat is transferred to 1.000 kg of water.

$$\Delta T = \frac{100.0 \text{ J}}{(4.18 \text{ J °C}^{-1} \text{ g}^{-1})(1.000 \text{ kg})}\left(\frac{1 \text{ kg}}{1000 \text{ g}}\right) = 0.0239 \text{ °C}$$

18. The volume of a cone is given by

$$V = \frac{1}{3}\pi r^2 h$$

where h is the height of the cone and r is the radius of its base. Find the volume of a cone if its radius is given as 0.443 m and its height is given as 0.542 m.

$$V = \frac{1}{3}\pi r^3 h = \frac{1}{3}\pi(0.443 \text{ m})^2(0.542 \text{ m}) = 0.111 \text{ m}^3$$

19. The volume of a sphere is equal to $\frac{4}{3}\pi r^3$ where r is the radius of the sphere. Assume that the earth is spherical with a radius of 3958.89 miles. (This is the radius of a sphere with the same volume as the earth, which is flattened at the poles by about 30 miles.) Find the volume of the earth in cubic miles and in cubic meters. Use a value of π with at least six digits and give the correct number of significant digits in your answer.

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(3958.89\ \mathrm{mi})^3$$
$$= 2.59508 \times 10^{11}\ \mathrm{mi}^3$$
$$(2.59508 \times 10^{11}\ \mathrm{mi}^3)\left(\frac{5280\ \mathrm{ft}}{1\ \mathrm{mi}}\right)^3\left(\frac{12\ \mathrm{in}}{1\ \mathrm{ft}}\right)^3$$
$$\times\left(\frac{0.0254\ \mathrm{m}}{1\ \mathrm{in}}\right)^3 = 1.08168 \times 10^{21}\ \mathrm{m}^3$$

20. Using the radius of the earth in the previous problem and the fact that the surface of the earth is about 70% covered by water, estimate the area of all of the bodies of water on the earth. The area of a sphere is equal to four times the area of a great circle, or $4\pi r^2$, where r is the radius of the sphere.

$$A \approx (0.7)4\pi r^2 = (0.7)4\pi(3958.89\ \mathrm{mi})^2$$
$$= 1.4 \times 10^8\ \mathrm{mi}^2$$

We give two significant digits since the use of 1 as a single digit would specify a possible error of about 50%. It is a fairly common practice to give an extra digit when the last significant digit is 1.

21. The hectare is a unit of land area defined to equal exactly 10,000 square meters, and the acre is a unit of land area defined so that 640 acres equals exactly one square mile. Find the number of square meters in 1.000 acre, and find the number of acres equivalent to 1.000 hectare.

$$1.000\ \mathrm{acre} = \left(\frac{(5280\ \mathrm{ft})^2}{640}\right)\left(\frac{12\ \mathrm{in}}{1\ \mathrm{ft}}\right)^2$$
$$\times\left(\frac{0.0254\ \mathrm{m}}{1\ \mathrm{in}}\right)^2 = 4047\ \mathrm{m}^2$$
$$1.000\ \mathrm{hectare} = (1.000\ \mathrm{hectare})\left(\frac{10000\ \mathrm{m}^2}{1\ \mathrm{hectare}}\right)$$
$$\times\left(\frac{1\ \mathrm{acre}}{4047\ \mathrm{m}^2}\right) = 2.471\ \mathrm{acre}$$

Chapter 2

Mathematical Functions

EXERCISES

Exercise 2.1. Enter a formula into cell $D2$ that will compute the mean of the numbers in cells $A2, B2$, and $C2$.

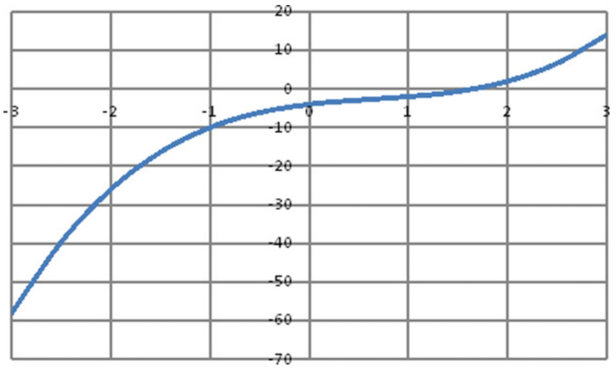
$$= (A2 + B2 + C2)/3$$

Exercise 2.2. Construct a graph representing the function

$$y(x) = x^3 - 2x^2 + 3x + 4 \tag{2.1}$$

Use Excel or Mathematica or some other software to construct your graph.

Here is the graph, constructed with Excel:



Exercise 2.3. Generate the negative logarithms in the short table of common logarithms.

x	$y = \log_{10}(x)$	x	$y = \log_{10}(x)$
1	0	0.1	−1
10	1	0.01	−2
100	2	0.001	−3
1000	3	0.0001	−4

$$0.1 = 1/10$$

$$\log(0.1) = -\log(10) = -1$$

$$0.01 = 1/100$$

$$\log(0.01) = -\log(100) = -2$$

$$0.001 = 1/1000$$

$$\log(0.001) = -\log(1000) = -3$$

$$0.0001 = 1/10000$$

$$\log(0.001) = -\log(10000) = -4$$

Exercise 2.4. Using a calculator or a spreadsheet, evaluate the quantity $(1+\frac{1}{n})^n$ for several integral values of n ranging from 1 to 1,000,000. Notice how the value approaches the value of e as n increases and determine the value of n needed to provide four significant digits.

Here is a table of values

x	$(1 + 1/n)^n$
1	2
2	2.25
5	2.48832
10	2.59374246
100	2.704813829
1000	2.716923932
10000	2.718145927
100000	2.718268237
1000000	2.718280469

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To twelve significant digits, the value of e is 2.71828182846. The value for $n = 1000000$ is accurate to six significant digits. Four significant digits are obtained with $n = 10000$.

Exercise 2.5. Without using a calculator or a table of logarithms, find the following:

a. $\ln(100.000) = \ln(10)\log_{10}(100.000)$
$= (2.30258509\cdots)(2.0000) = 4.60517$

b. $\ln(0.0010000) = \ln(10)\log_{10}(0.0010000)$
$= (2.30258509\cdots)(-3.0000) = -6.90776$

c. $\log_{10}(e) = \dfrac{\ln(e)}{\ln(10)} = \dfrac{1}{2.30258509\cdots} = 0.43429\cdots$

Exercise 2.6. For a positive value of b find an expression in terms of b for the change in x required for the function e^{bx} to double in size.

$$\frac{f(x+\Delta x)}{f(x)} = 2 = \frac{e^{b(x+\Delta x)}}{e^{bx}} = e^{b\Delta x}$$

$$\Delta x = \frac{\ln(2)}{b} = \frac{0.69315\cdots}{b}$$

Exercise 2.7. A reactant in a first-order chemical reaction without back reaction has a concentration governed by the same formula as radioactive decay,

$$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt},$$

where $[\mathrm{A}]_0$ is the concentration at time $t = 0$, $[\mathrm{A}]_t$ is the concentration at time t, and k is a function of temperature called the rate constant. If $k = 0.123\ \mathrm{s}^{-1}$ find the time required for the concentration to drop to 21.0% of its initial value.

$$t = \left(\frac{1}{k}\right)\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}\right) = \left(\frac{1}{0.123\ \mathrm{s}^{-1}}\right)\ln\left(\frac{100.0}{21.0}\right)$$
$$= 12.7\ \mathrm{s}$$

Exercise 2.8. Using a calculator, find the value of the cosine of 15.5° and the value of the cosine of 375.5°. Display as many digits as your calculator is able to display. Check to see if your calculator produces any round-off error in the last digit. Choose another pair of angles that differ by 360° and repeat the calculation. Set your calculator to use angles measured in radians. Find the value of $\sin(0.3000)$. Find the value of $\sin(0.3000 + 2\pi)$. See if there is any round-off error in the last digit.

$$\begin{aligned}
\cos(15.5^\circ) &= 0.96363045321 \\
\cos(375.5^\circ) &= 0.96363045321 \\
\sin(0.3000) &= 0.29552020666 \\
\sin(0.3000 + 2\pi) &= \sin(6.58318530718) \\
&= 0.29552020666
\end{aligned}$$

There is no round-off error to 11 digits in the calculator that was used.

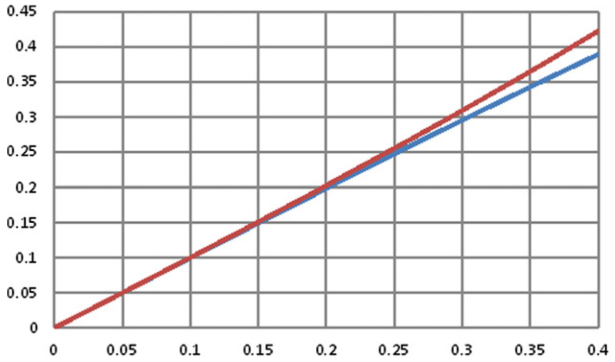
Exercise 2.9. Using a calculator and displaying as many digits as possible, find the values of the sine and cosine of 49.500°. Square the two values and add the results. See if there is any round-off error in your calculator.

$$\sin(49.500^\circ) = 0.7604059656$$

$$\cos(49.500^\circ) = 0.64944804833$$

$$(0.7604059656)^2 + (0.64944804833)^2 = 1.00000000000$$

Exercise 2.10. Construct an accurate graph of $\sin(x)$ and $\tan(x)$ on the same graph for values of x from 0 to 0.4 rad and find the maximum value of x for which the two functions differ by less than 1%.



The two functions differ by less than 1% at 0.14 rad. Notice that at 0.4 rad, $\sin(x) \prec x \prec \tan(x)$ and that the three quantities differ by less than 10%.

Exercise 2.11. For an angle that is nearly as large as $\pi/2$, find an approximate equality similar to Eq. (2.36) involving $(\pi/2) - \alpha$, $\cos(\alpha)$, and $\cot(\alpha)$.

Construct a right triangle with angle with the angle $(\pi/2) - \alpha$, where α is small. The triangle is tall, with a small value of x (the horizontal leg) and a larger value of y (the vertical leg). Let r be the hypotenuse, which is nearly equal to y.

$$\cos((\pi/2) - \alpha) = \frac{x}{r}$$

$\cot((\pi/2) - \alpha) = \frac{x}{y} \approx \frac{x}{r}$. The measure of the angle in radians is equal to the arc length subtending the angle α divided by r and is very nearly equal to x/r. Therefore

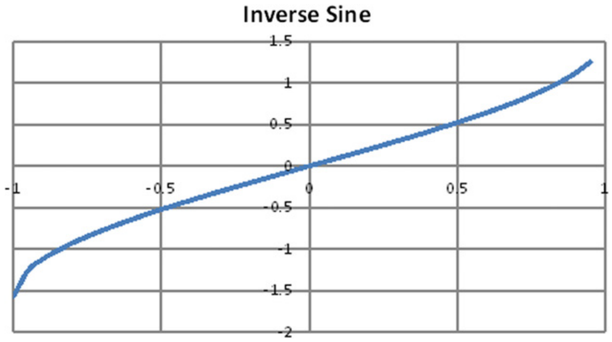
$$\cos((\pi/2) - \alpha) \approx \alpha$$

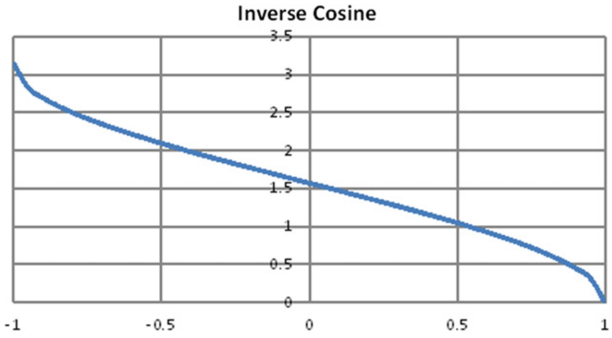
$$\cot((\pi/2) - \alpha) \approx \alpha$$

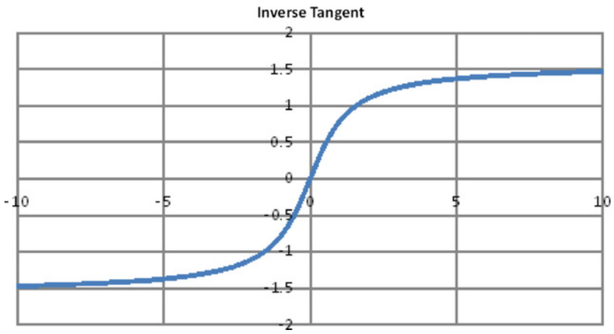
$$\cos((\pi/2) - \alpha) \approx \cot((\pi/2) - \alpha)$$

Exercise 2.12. Sketch graphs of the arcsine function, the arccosine function, and the arctangent function. Include only the principal values.

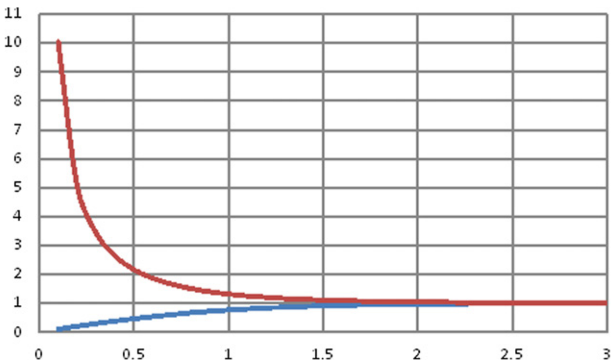
Here are accurate graphs:







Exercise 2.13. Make a graph of $\tanh(x)$ and $\coth(x)$ on the same graph for values of x ranging from 0.1 to 3.0.



Exercise 2.14. Determine the number of significant digits in $\sin(95.5°)$.

We calculate $\sin(95.45°)$ and $\sin(95.45°)$. Using a calculator that displays 8 digits, we obtain

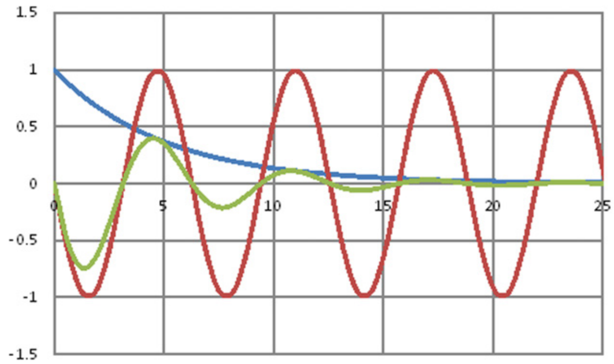
$$\sin(95.45°) = 0.99547946$$

$$\sin(95.55°) = 0.99531218$$

We report the sine of 95.5° as 0.9954, specifying four significant digits, although the argument of the sine was given with three significant digits. We have followed the common policy of reporting a digit as significant if it might be incorrect by one unit.

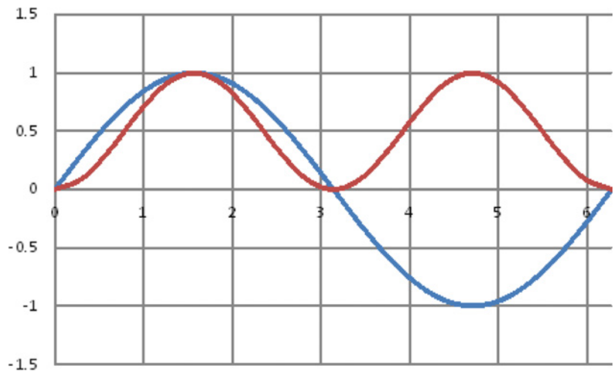
Exercise 2.15. Sketch rough graphs of the following functions. Verify your graphs using Excel or Mathematica.

a. $e^{-x/5}\sin(x)$. Following is a graph representing each of the factors and their product:



b. $\sin^2(x) = [\sin(x)]^2$

Following is a graph representing $\sin(x)$ and $\sin^2(x)$.



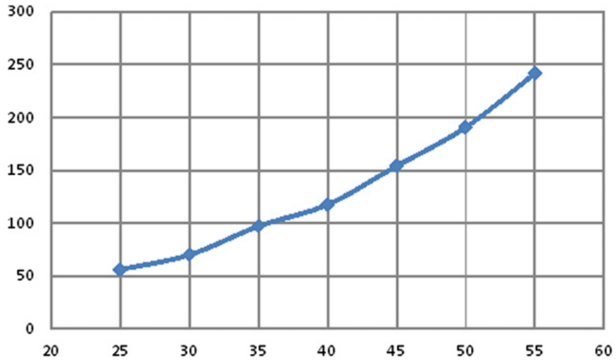
PROBLEMS

1. The following is a set of data for the vapor pressure of ethanol taken by a physical chemistry student. Plot these points by hand on graph paper, with the temperature on the horizontal axis (the abscissa) and

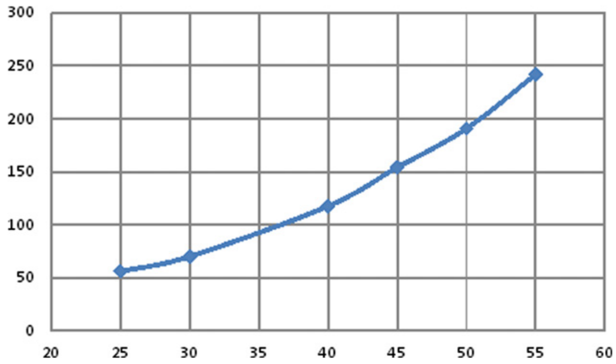
the vapor pressure on the vertical axis (the ordinate). Decide if there are any bad data points. Draw a smooth curve nearly through the points, disregarding any bad points. Use Excel to construct another graph and notice how much work the spreadsheet saves you.

Temperature/°C	Vapor pressure/torr
25.00	55.9
30.00	70.0
35.00	97.0
40.00	117.5
45.00	154.1
50.00	190.7
55.00	241.9

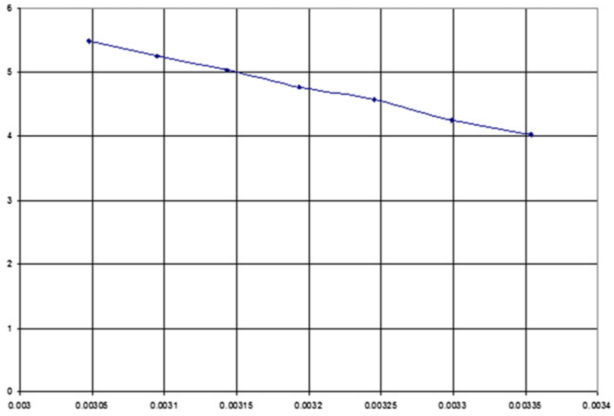
Here is a graph constructed with Excel:



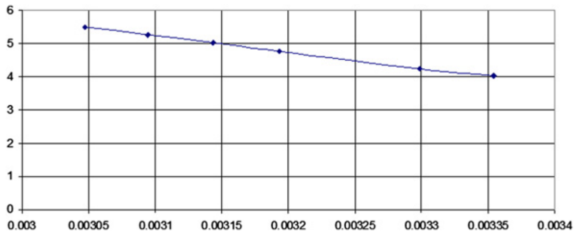
The third data point might be suspect. Here is a graph omitting that data point:



2. Using the data from the previous problem, construct a graph of the natural logarithm of the vapor pressure as a function of the reciprocal of the Kelvin temperature. Why might this graph be more useful than the graph in the previous problem?



This graph might be more useful than the first graph because the function is nearly linear. However, the third data point still lies off the curve. Here is a graph with that data point omitted.



Thermodynamic theory implies that it should be nearly linear if there were no experimental error.

3. A reactant in a first-order chemical reaction without back reaction has a concentration governed by the same formula as radioactive decay,

$$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt},$$

where $[\mathrm{A}]_0$ is the concentration at time $t = 0$, $[\mathrm{A}]_t$ is the concentration at time t, and k is a function of temperature called the rate constant. If $k = 0.232\ \mathrm{s}^{-1}$ at 298.15 K find the time required for the concentration to drop to 33.3% of its initial value at a constant temperature of 298.15 K.

$$t = \frac{\ln\left([\mathrm{A}]_0/[\mathrm{A}]_t\right)}{k} = \frac{\ln(1/0.333)}{0.232\ \mathrm{s}^{-1}} = 4.74\ \mathrm{s}$$

4. Find the value of each of the hyperbolic trigonometric functions for $x = 0$ and $x = \pi/2$. Compare these values with the values of the ordinary (circular) trigonometric functions for the same values of the independent variable.

Here are two table of values:

x	sinh(x)	cosh(x)	tanh(x)	csch(x)	sech(x)	coth(x)
0	0	1	0	∞	1	∞
$\pi/2$	2.3013	2.5092	0.91715	0.43454	0.39854	1.09033

x	sin(x)	cos(x)	tan(x)	csc(x)	sec(x)	cot(x)
0	0	1	0	∞	0	∞
$\pi/2$	1	0	∞	1	∞	0

5. Express the following with the correct number of significant digits. Use the arguments in radians:

a. tan (0.600)

$$\tan(0.600) = 0.684137$$
$$\tan(0.5995) = 0.683403$$
$$\tan(0.60005) = 0.684210$$

We report tan (0.600) = 0.684. If a digit is probably incorrect by 1, we still treat it as significant.

b. sin (0.100)

$$\sin(0.100) = 0.099833$$
$$\sin(0.1005) = 0.100331$$
$$\sin(0.0995) = 0.099336$$

We report sin (0.100) = 0.100.

c. cosh (12.0)

$$\cosh(12.0) = 81377$$
$$\cosh(12.05) = 85550$$
$$\cosh(11.95) = 77409$$

We report cosh $(12.0) = 8 \times 10^4$. There is only one significant digit.

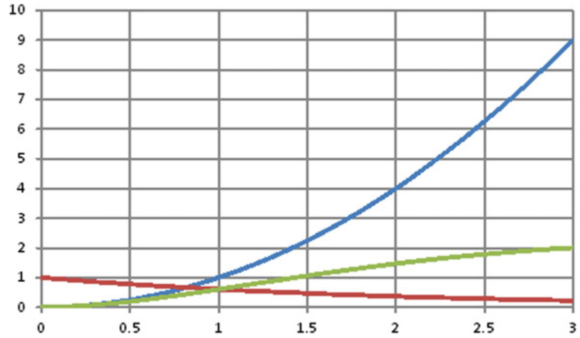
d. sinh (10.0)

$$\sinh(10.0) = 11013$$
$$\sinh(10.01) = 11578$$
$$\sinh(9.995) = 10476$$

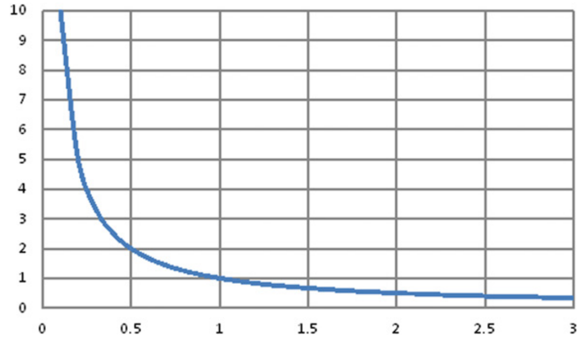
We report sinh $(10.0) = 11000 = 1.1 \times 10^4$

6. Sketch rough graphs of the following functions. Verify your graphs using Excel or Mathematica:

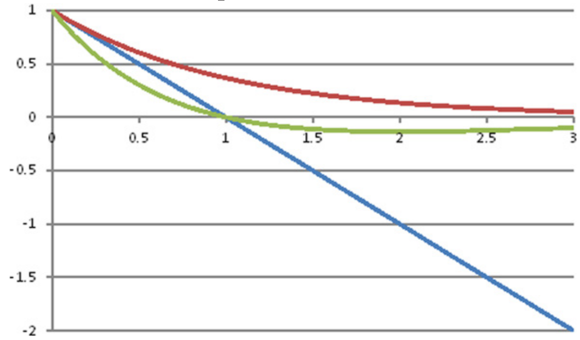
a. $x^2e^{-x/2}$ Following is a graph of the two factors and their product.



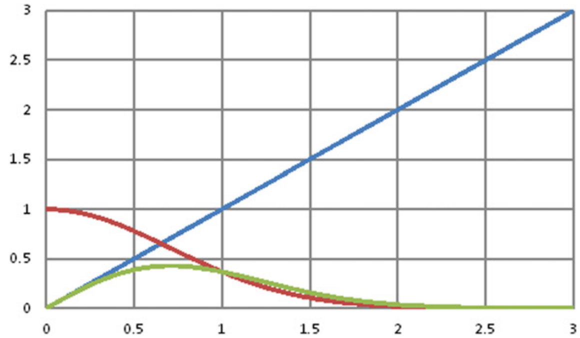
b. $1/x^2$ Following is the graph:



c. $(1-x)e^{-x}$ Following is a graph showing each factor and their product.



d. xe^{-x^2} Following is a graph showing the two factors and their product.



7. Tell where each of the following functions is discontinuous. Specify the type of discontinuity:

a. tan (x) Infinite discontinuities at $x = \pi/2$, $x = 3\pi/2$, $x = 5\pi/2, \cdots$

b. csc (x) Infinite discontinuities at $x = 0$, $x = \pi$, $x = 2\pi, \cdots$

c. $|x|$ Continuous everywhere, although there is a sharp change of direction at $x = 0$.

8. Tell where each of the following functions is discontinuous. Specify the type of discontinuity:

a. cot (x) Infinite discontinuities at $x = 0, x = \pi$, $x = 2\pi, \cdots$

b. sec (x) Infinite discontinuities at $x = \pi/2$, $x = 3\pi/2$, $x = 5\pi/2, \cdots$

c. ln $(x-1)$ Infinite discontinuity at $x = 1$, function not defined for $x \prec 1$.

9. If the two ends of a completely flexible chain (one that requires no force to bend it) are suspended at the same height near the surface of the earth, the curve representing the shape of the chain is called a catenary. It can be shown[1] that the catenary is represented by

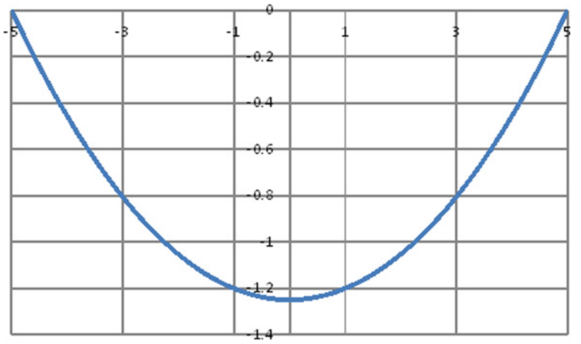
$$y = a \cosh\left(\frac{x}{a}\right)$$

where

$$a = \frac{T}{g\rho}$$

and where ρ is the mass per unit length, g is the acceleration due to gravity, and T is the tension force on the chain. The variable x is equal to zero at the center of the chain. Construct a graph of this function such that the distance between the two points of support is 10.0 m and the mass per unit length is 0.500 kg m^{-1}, and the tension force is 50.0 N.

$$a = \frac{T}{g\rho} = \frac{50.0 \text{ kg m s}^2}{(9.80 \text{ m}^2 \text{ s}^{-2})(0.500 \text{ kg m}^{-1})} = 10.20 \text{ m}$$
$$y = (10.20 \text{ m}) \cosh(x/10.20 \text{ m})$$



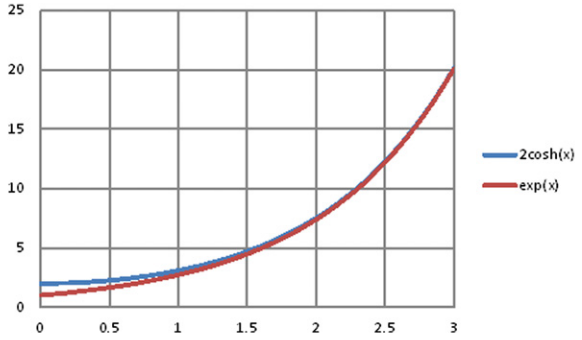
For this graph, we have plotted $y - 11.4538$ such that this quantity vanishes at the ends of the chain.

10. For the chain in the previous problem, find the force necessary so that the center of the chain is no more than 0.500 m lower than the ends of the chain.

By trial and error, we found that the center of the chain is 0.499 m below the ends when $a = 25.5$ m. This corresponds to

$$T = g\rho a = (9.80 \text{ m s}^{-2})(0.500 \text{ kg m}^{-1})(25.5 \text{ m}) = 125 \text{ N}$$

11. Construct a graph of the two functions: 2 cosh (x) and e^x for values of x from 0 to 3. At what minimum value of x do the two functions differ by less than 1%?



By inspection in a column of values of the difference, the two functions differ by less than 1% at $x = 2.4$.

12. Verify the trigonometric identity

$$\sin(x + y) = \sin(x)\cos(y) + \cos(x)\sin(y)$$

for the angles $x = 1.00000$ rad, $y = 2.00000$ rad. Use as many digits as your calculator will display and check for round-off error.

$$\sin(3.00000) = 0.14112000806$$
$$\sin(1.00000)\cos(2.00000) + \cos(1.00000) \times \sin(2.00000) = 0.14112000806$$

There was no round-off error in the calculator that was used.

13. Verify the trigonometric identity

$$\cos(2x) = 1 - 2\sin^2(x)$$

for $x = 0.50000$ rad. Use as many digits as your calculator will display and check for round-off error.

$$\cos(1.00000) = 0.54030230587$$
$$1 - 2\sin^2(0.50000) = 1 - 0.45969769413 = 0.54030230587$$

There was no round-off error to 11 significant digits in the calculator that was used.

[1] G. Polya, Mathematical Methods in Science, The Mathematical Association of America, 1977, pp. 178ff.

Chapter 3

Problem Solving and Symbolic Mathematics: Algebra

EXERCISES

Exercise 3.1. Write the following expression in a simpler form:

$$B=\frac{(x^2+2x)^2-x^2(x-2)^2+12x^4}{6x^3+12x^4}.$$

$$\begin{aligned}B&=\frac{x^2(x^2+4x+4)-x^2(x^2-4x+4)+12x^4}{6x^3+12x^4}\\&=\frac{x^4+4x^3+4x^2-x^4+4x^3-4x^2+12x^4}{6x^3+12x^4}\\&=\frac{12x^4+8x^3}{6x^3+12x^4}=\frac{12x+8}{12x+6}=\frac{6x+4}{6x+3}\end{aligned}$$

Exercise 3.2. Manipulate the van der Waals equation into an expression for P in terms of T and V_{m}. Since the pressure is independent of the size of the system (it is an intensive variable), thermodynamic theory implies that it can depend on only two independent intensive variables.

$$\begin{aligned}\left(P+\frac{a}{V_{\mathrm{m}}^2}\right)(V_{\mathrm{m}}-b)&=RT\\P+\frac{a}{V_{\mathrm{m}}^2}&=\frac{RT}{V_{\mathrm{m}}-b}\\P&=\frac{RT}{V_{\mathrm{m}}-b}-\frac{a}{V_{\mathrm{m}}^2}\end{aligned}$$

Exercise 3.3. a. Find x and y if $\rho=6.00$ and $\phi=\pi/6$ radians

$$\begin{aligned}x&=(6.00)\cos(\pi/6)=(6.00)(0.866025)=5.20\\y&=\rho\sin(\phi)=(6.00)(0.500)=3.00\end{aligned}$$

b. Find ρ and ϕ if $x=5.00$ and $y=10.00$.

$$\begin{aligned}\rho&=\sqrt{x^2+y^2}=\sqrt{125.0}=11.18\\\phi&=\arctan(y/x)=\arctan(2.00)=1.107\text{ rad}\\&=63.43^\circ\end{aligned}$$

Exercise 3.4. Find the spherical polar coordinates of the point whose Cartesian coordinates are (2.00, 3.00, 4.00).

$$\begin{aligned}r&=\sqrt{(2.00)^2+(3.00)^2-(4.00)^2}=\sqrt{29.00}=5.39\\\phi&=\arctan\left(\frac{3.00}{2.00}\right)=0.98279\text{ rad}=56.3^\circ\\\theta&=\arccos\left(\frac{4.00}{5.39}\right)=0.733\text{ rad}=42.0^\circ\end{aligned}$$

Exercise 3.5. Find the Cartesian coordinates of the point whose cylindrical polar coordinates are $\rho=25.00, \phi=60.0^\circ$, $z=17.50$

$$\begin{aligned}x&=\rho\cos(\phi)=25.00\cos(60.0^\circ)\\&=25.00\times0.500=12.50\\y&=\rho\sin(\phi)=25.00\sin(60.0^\circ)\\&=25.00\times0.86603=21.65\\z&=17.50\end{aligned}$$

Exercise 3.6. Find the cylindrical polar coordinates of the point whose Cartesian coordinates are (−2.000, −2.000, 3.000).

$$\begin{aligned}\rho&=\sqrt{(-2.00)^2+(-2.00)^2}=2.828\\\phi&=\arctan\left(\frac{-2.00}{-2.00}\right)=0.7854\text{ rad}=45.0^\circ\\z&=3.000\end{aligned}$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00027-6

Exercise 3.7. Find the cylindrical polar coordinates of the point whose spherical polar coordinates are $r = 3.00$, $\theta = 30.00°$, $\phi = 45.00°$.

$$\begin{aligned} z &= r\cos(\theta) = (3.00)\cos(30.00°) = 3.00 \times 0.86603 \\ &= 2.60 \\ \rho &= r\sin(\theta) = (3.00)\sin(30.00°) = (3.00)(0.500) \\ &= 1.50 \\ \phi &= 45.00° \end{aligned}$$

Exercise 3.8. Simplify the expression

$$(4+6i)(3+2i)+4i$$

$$(4+6i)(3+2i)+4i = 12+18i+8i-12+4i = 30i$$

Exercise 3.9. Express the following complex numbers in the form $re^{i\phi}$:

a. $z = 4.00 + 4.00i$

$$\begin{aligned} r &= \sqrt{32.00} = 5.66 \\ \phi &= \arctan\left(\frac{4.00}{4.00}\right) = 0.785 \\ z &= 4.00 + 4.00i = 5.66e^{0.785i} \end{aligned}$$

b. $z = -1.00$

$$z = -1 = e^{\pi i}$$

Exercise 3.10. Express the following complex numbers in the form $x + iy$

a. $z = 3e^{\pi i/2}$

$$\begin{aligned} x &= r\cos(\phi) = 3\cos(\pi/2) = 3\times 0 = 0 \\ y &= r\sin(\phi) = 3\sin(\pi/2) = 3\times 1 = 3 \\ z &= 3i \end{aligned}$$

b. $z = e^{3\pi i/2}$

$$\begin{aligned} x &= r\cos(\phi) = \cos(3\pi/2) = 0 \\ y &= r\sin(\phi) = \sin(3\pi/2) = -1 \\ z &= -i \end{aligned}$$

Exercise 3.11. Find the complex conjugates of

a. $A = (x+iy)^2 - 4e^{ixy}$

$$\begin{aligned} A &= x^2 + 2ixy + y^2 - 4e^{ixy} \\ A^* &= x^2 - 2ixy + y^2 - 4e^{-ixy} \\ &= (x-iy)^2 - 4e^{-ixy} \end{aligned}$$

Otherwise by changing the sign in front of every i:

$$A^* = (x-iy)^2 - 4e^{-ixy}$$

b. $B = (3+7i)^3 - (7i)^2$.

$$B^* = (3-7i)^3 - (-7i)^2 = (3-7i)^3 - (7)^2$$

Exercise 3.12. Write a complex number in the form $x+iy$ and show that the product of the number with its complex conjugate is real and nonnegative

$$(x+iy)(x-iy) = x^2 + ixy - ixy + y^2 = x^2 + y^2$$

The square of a real number is real and nonnegative, and x and y are real.

Exercise 3.13. If $z = (3.00 + 2.00i)^2$, find $R(z)$, $I(z)$, r, and ϕ.

$$z = 9.00 + 6.00i - 4.00 = 5.00 + 6.00i$$

$$\begin{aligned} R(z) &= 5.00 \\ I(z) &= 6.00 \\ r &= \sqrt{25.00 + 36.00} = 7.781 \\ \phi &= \arctan(6.00/5.00) = 0.876 \text{ rad} = 50.2° \end{aligned}$$

Exercise 3.14. Find the square roots of $z = 4.00 + 4.00i$. Sketch an Argand diagram and locate the roots on it.

$$\begin{aligned} z &= re^{i\phi} \\ r &= \sqrt{32.00} = 5.657 \\ \phi &= \arctan(1.00) = 0.785398 \text{ rad} = 45.00° \end{aligned}$$

$$\sqrt{z} = \begin{cases} \sqrt{5.657}e^{0.3927i} \\ \sqrt{5.657}\exp\left[\left(\frac{0.785398+2\pi}{2}\right)i\right] = \sqrt{5.657}e^{3.534i} \end{cases}$$

To sketch the Argand diagram, we require the real and imaginary parts. For the first possibility

$$\begin{aligned} \sqrt{z} &= \sqrt{5.657}(\cos(22.50°)) + i\sin(22.50°) \\ &= \sqrt{5.657}(0.92388 + i(0.38268) \\ &= 2.1973 + 0.91019i \end{aligned}$$

For the second possibility

$$\begin{aligned} \sqrt{z} &= \sqrt{5.657}(\cos(202.50°)) + i\sin(202.50°) \\ &= \sqrt{5.657}(-0.92388 + i(-0.38268) \\ &= -2.1973 - 0.91019i \end{aligned}$$

Exercise 3.15. Find the four fourth roots of -1.

$$\begin{aligned} -1 &= e^{\pi i}, e^{3\pi i}, e^{5\pi i}, e^{7\pi i} \\ \sqrt[4]{e^{\pi i}} &= e^{\pi i/4}, e^{3\pi i/4}, e^{5\pi i/4}, e^{7\pi i/4} \end{aligned}$$

Exercise 3.16. Estimate the number of house painters in Chicago.

The 2010 census lists a population of 2,695,598 for the city of Chicago, excluding surrounding areas. Assume that about 20% of Chicagoans live in single-family houses or duplexes that would need exterior painting. With an average family size of four persons for house-dwellers, this would give about 135,000 houses. Each house would be painted about once in six or eight years, giving roughly 20,000 house-painting jobs per year. A crew of two painters might paint a house in one week, so that a crew of two painters could paint about 50 houses in a year. This gives about 400 two-painter crews, or 800 house painters in Chicago.

PROBLEMS

1. Manipulate the van der Waals equation into a cubic equation in V_{m}. That is, make a polynomial with terms proportional to powers of V_{m} up to V_{m}^3 on one side of the equation.

$$\left(P + \frac{a}{V_{\mathrm{m}}^2}\right)(V_{\mathrm{m}} - b) = RT$$

Multiply by V_{m}^2

$$\begin{aligned}(PV_{\mathrm{m}}^2 + a)(V_{\mathrm{m}} - b) &= RTV_{\mathrm{m}}^2 \\ PV_{\mathrm{m}}^3 + aV_{\mathrm{m}} - bPV_{\mathrm{m}}^2 - ab &= RTV_{\mathrm{m}}^2 \\ PV_{\mathrm{m}}^3 - (b + RT)V_{\mathrm{m}}^2 + aV_{\mathrm{m}} - ab &= 0\end{aligned}$$

2. Find the value of the expression

$$\frac{3(2+4)^2 - 6(7 + |-17|)^3 + \left(\sqrt{37 - |-1|}\right)^3}{(1+2^2)^4 - (|-7| + 6^3)^2 + \sqrt{12 + |-4|}}$$

$$\begin{aligned}&\frac{3(2+4)^2 - 6(7|-17|)^3 + \left(\sqrt{37 - |-1|}\right)^3}{(1+2^2)^4 - (|-7| + 6^3)^2 + \sqrt{12 + |-4|}} \\ &= \frac{3(6)^2 - 6(24)^3 + \left(\sqrt{36}\right)^3}{(5)^4 - (223)^2 + \sqrt{16}} \\ &= \frac{72 - 82944 + 216}{625 - 49729 + 4} = \frac{-82656}{-49100} = 1.683\end{aligned}$$

3. A Boy Scout finds a tall tree while hiking and wants to estimate its height. He walks away from the tree and finds that when he is 45 m from the tree, he must look upward at an angle of 32° to look at the top of the tree. His eye is 1.40 m from the ground, which is perfectly level. How tall is the tree?

$$\begin{aligned}h &= (45\ \mathrm{m})\tan(32°) + 1.40\ \mathrm{m} = 28.1\ \mathrm{m} + 1.40\ \mathrm{m} \\ &= 29.5\ \mathrm{m} \approx 3\bar{0}\ \mathrm{m}\end{aligned}$$

The zero in 30 m is significant, which we indicated with a bar over it.

4. The equation $x^2 + y^2 + z^2 = c^2$ where c is a constant, represents a surface in three dimensions. Express the equation in spherical polar coordinates. What is the shape of the surface?

$$x^2 + y^2 + z^2 = r^2 = c^2$$

This represents a sphere with radius c.

5. Express the equation $y = b$, where b is a constant, in plane polar coordinates.

$$\begin{aligned}y &= \rho\sin(\phi) = b \\ \rho &= \frac{b}{\sin(\phi)} = b\csc(\phi)\end{aligned}$$

6. Express the equation $y = mx + b$, where m and b are constants, in plane polar coordinates.

$$\begin{aligned}\rho\sin(\phi) &= m\rho\cos(\phi) + b \\ \rho\tan(\phi) &= m\rho + b\sec(\phi) \\ \rho[\tan(\phi) - m] &= b\sec(\phi) \\ \rho &= \frac{b\sec(\phi)}{[\tan(\phi) - m]}\end{aligned}$$

7. Find the values of the plane polar coordinates that correspond to $x = 3.00$, $y = 4.00$.

$$\begin{aligned}\rho &= \sqrt{9.00 + 16.00} = 5.00 \\ \phi &= \arctan\left(\frac{4.00}{3.00}\right) = 53.1° = 0.927\ \mathrm{rad}\end{aligned}$$

8. Find the values of the Cartesian coordinates that correspond to $r = 5.00$, $\theta = 45.0°$, $\phi = 135.0°$.
9. A surface is represented in cylindrical polar coordinates by the equation $z = \rho^2$. Describe the shape of the surface. This equation represents a paraboloid of revolution, produced by revolving a parabola around the z axis.
10. The solutions to the Schrödinger equation for the electron in a hydrogen atom have three quantum numbers associated with them, called n, l, and m, and these solutions are denoted by ψ_{nlm}.

   a. The ψ_{210} function is given by

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos(\theta)$$

   where $a_0 = 0.529 \times 10^{-10}$ m is called the Bohr radius. Write this function in terms of Cartesian coordinates.

$$\begin{aligned}\cos(\theta) &= z \\ \psi_{210} &= \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \\ &\quad\times\frac{z}{a_0}\exp\left[-\frac{(x^2+y^2+z^2)^{1/2}}{2a_0}\right]\end{aligned}$$

b. The ψ_{211} function is given by

$$\psi_{211} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin(\theta)e^{i\phi}$$

Write an expression for the magnitude of the ψ_{211} function.

$$\begin{aligned}|\psi_{211}| &= (\psi_{211}\psi_{211}^*)^{1/2} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\\ &\quad\times\frac{r}{a_0}e^{-r/2a_0}\sin(\theta)(e^{i\phi}e^{-i\phi})^{1/2}\\ &= \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin(\theta)\end{aligned}$$

c. The ψ_{211} function is sometimes called ψ_{2p1}. Write expressions for the real and imaginary parts of the function, which are proportional to the related functions called ψ_{2px} and ψ_{2py}.

$$\begin{aligned}R(\psi_{211}) &= \frac{1}{2}\left(\psi_{211}+\psi_{211}^*\right)\\ &= \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin(\theta)\\ &\quad\times\left(\frac{1}{2}\right)\left(e^{i\phi}+e^{-i\phi}\right)\\ &= \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\\ &\quad\times\sin(\theta)\cos(\phi)\end{aligned}$$

$$\begin{aligned}I(\psi_{211}) &= \frac{1}{2i}\left(\psi_{211}-\psi_{211}^*\right)\\ &= \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin(\theta)\\ &\quad\times\left(\frac{1}{2i}\right)(e^{i\phi}-e^{-i\phi})\\ &= \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\\ &\quad\times\sin(\theta)\sin(\phi)\end{aligned}$$

11. Find the complex conjugate of the quantity $e^{2.00i}+3e^{i\pi}$

$$\begin{aligned}e^{2.00i}+3e^{i\pi} &= e^{2.00i}-3 = \cos(2.00)\\ &\quad+i\sin(2.00)-3\\ (e^{2.00i}+3e^{i\pi})^* &= \cos(2.00)-i\sin(2.00)-3\\ &= e^{-2.00i}-3\end{aligned}$$

12. Find the sum of $4.00e^{3.00i}$ and $5.00e^{2.00i}$.

$$\begin{aligned}4.00e^{3.00i} &= (4.00)[\cos(3.00)+i\sin(3.00)]\\ &= (4.00)(-0.98999+0.14112i)\\ &= -3.95997+0.56448i\\ 5.00e^{2.00i} &= (5.00)****[\cos(2.00]+i\sin(2.00)\\ &= (5.00)(-0.41615+0.90930i)\\ &= -2.08075+4.54650i\\ 4.00e^{3.00i}&+5.00e^{2.00i}\\ &= -6.04+5.11i\end{aligned}$$

13. Find the difference $3.00e^{\pi i}-2.00e^{2\pi i}$.

$$3.00e^{\pi i}-2.00e^{2\pi i} = -3.00-2.00 = 5.00$$

14. Find the three cube roots of $z = 3.000+4.000i$.

$$\begin{aligned}r &= \sqrt{9.000+16.000} = 5.000\\ \phi &= \arctan(4.000/3.000) = 0.92730\text{ rad}\\ z &= \begin{cases}5.000e^{i\phi} = 5.000e^{0.92730i}\\ 5.000e^{(2\pi+\phi)} = 5.000e^{7.21048i}\\ 5.000e^{(4\pi+\phi)} = 5.000e^{13.49367}\end{cases}\\ z^{1/3} &= \begin{cases}1.710e^{0.30910i}\\ 1.710e^{2.40349i}\\ 1.710e^{4.49789i}\end{cases}\end{aligned}$$

15. Find the four fourth roots of $3.000i$.

$$3.000i = \begin{cases}3.000e^{\pi i/2}\\ 3.000e^{5\pi i/2}\\ 3.000e^{9\pi i/2}\\ 3.000e^{13\pi i/2}\end{cases}$$

$$\sqrt[4]{3.000i} = \begin{cases}\sqrt[4]{3.000}e^{\pi i/8} = 1.316e^{\pi i/8}\\ \sqrt[4]{3.000}e^{5\pi i/8} = 1.316e^{5\pi i/8}\\ \sqrt[4]{3.000}e^{9\pi i/8} = 1.316e^{9\pi i/8}\\ \sqrt[4]{3.000}e^{13\pi i/8} = 1.316e^{13\pi i/8}\end{cases}$$

16. Find the real and imaginary parts of

$$z = (3.00+i)^3+(6.00+5.00i)^2$$

Find z^*.

$$\begin{aligned}(3.00+i)^3 &= (3.00+i)(9.00+6.00i-1)\\ &= 27.00+18.00i-3.00+9.00i\\ &\quad-6.00-i = 18.00+26.00i\\ (6.00+5.00i)^2 &= 36.00+60.00i-25.00\\ &= 11.00+60.00i\\ (3.00+i)^3&+(6.00+5.00i)^2\\ &= 29.00+86.00i\\ z^* &= 29.00-86.00i\end{aligned}$$

17. If $z = \left(\frac{3+2i}{4+5i}\right)^2$, find $R(z)$, $I(z)$, r, and ϕ.

$$
\begin{aligned}
(4+5i)^{-1} &= \frac{4-5i}{16+25} = \frac{4-5i}{41} \\
\frac{3+2i}{4+5i} &= \left(\frac{4-5i}{41}\right)(3+2i) \\
&= \frac{12}{41} + \left(\frac{-15+8}{41}\right)i + \frac{10}{41} \\
&= \frac{22}{41} - \frac{7i}{41} \\
\left(\frac{22}{41} - \frac{7i}{41}\right)^2 &= \left(\frac{22}{41}\right)^2 \\
&\quad - \left(\frac{2\times 22\times 7}{(41)^2}\right)i + \left(\frac{5}{41}\right)^2 \\
&= 0.43378 - 0.18322i
\end{aligned}
$$

$$
\begin{aligned}
R(z) &= 0.43378 \\
I(z) &= -0.18322
\end{aligned}
$$

$$
\begin{aligned}
r &= \sqrt{(0.43378)^2 + (0.18322)^2} = 0.47079 \\
\phi &= \arctan\left(\frac{-0.18322}{0.43378}\right) = \arctan(-0.42238) \\
&= -0.39965
\end{aligned}
$$

The principal value of the arctangent is in the fourth quadrant, equal to -0.39965 rad. Since ϕ ranges from 0 to 2π, we subtract 0.39965 from 2π to get

$$\phi = 5.8835 \text{ rad}$$

18. Obtain the famous formulas

$$\boxed{\cos(\phi) = \frac{e^{i\phi} + e^{-i\phi}}{2} = R(e^{i\phi})}$$

$$\boxed{\sin(\phi) = \frac{e^{i\phi} - e^{-i\phi}}{2i} = I(e^{i\phi})}$$

If $z = e^{i\phi}$ The real part is obtained from

$$R(z) = \frac{z+z^*}{2} = \frac{e^{i\phi} + e^{-i\phi}}{2}$$

and the imaginary part is obtained from

$$I(z) = \frac{z-z^*}{2i} = \frac{e^{i\phi} - e^{-i\phi}}{2i}$$

in agreement with the formula $e^{i\phi} = \cos(\phi) + i\sin(\phi)$

19. Estimate the number of grains of sand on the beaches of the major continents of the earth. Exclude islands and inland bodies of water.

Assume that the earth has seven continents with an average radius of 2000 km. Since the coastlines are somewhat irregular, assume that each continent has a coastline of roughly 10000 km $= 1 \times 10^7$ m for a total coastline of 7×10^7 m. Assume that the average stretch of coastline has sand roughly 5 m deep and 50 m wide. This gives a total volume of beach sand of 1.75×10^{10} m^3. Assume that the average grain of sane is roughly 0.3 mm in diameter, so that each cubic millimeter contains roughly 30 grains of sand. This is equivalent to 3×10^{10} grains per cubic meter, so that we have roughly 5×10^{20} grains of sand. If we were to include islands and inland bodies of water, we would likely have a number of grains of sand nearly equal to Avogadro's constant.

20. A gas has a molar volume of 20 liters. Estimate the average distance between nearest-neighbor molecules.

Assume that each molecule is found in a cube such that 20 liters is divided into a number of cubes equal to Avogadro's constant:

$$\text{volume of a cube} = \frac{(20\ \text{l})\left(\frac{1\ \text{m}^3}{1000\ \text{l}}\right)}{6 \times 10^{23}} = 3 \times 10^{-26}\ \text{m}^3$$

The length of the side of the cube is roughly the average distance between molecules:

$$
\begin{aligned}
\text{average distance} &= \left(3 \times 10^{-26}\ \text{m}^3\right)^{1/3} = 3 \times 10^{-9}\ \text{m} \\
&= 30\ \text{Å}
\end{aligned}
$$

This is a reasonable value, since it is roughly ten times as large as a molecular diameter.

21. Estimate the number of blades of grass in a lawn with an area of 1000 square meters.

Assume approximately 10 blades per square centimeter.

$$
\begin{aligned}
\mathit{number} &= (10\ \text{cm}^{-2})\left(\frac{100\ \text{cm}}{1\ \text{m}}\right)^2 (1000\ \text{m}^2) \\
&= 1 \times 10^8
\end{aligned}
$$

22. Since in its early history the earth was too hot for liquid water to exist on it, it has been hypothesized that all of the water on the earth came from collisions of comets with the earth. Assume an average diameter for the head of a comet and assume that it is completely composed of water ice. Estimate the volume of water on the earth and estimate how many comets would have collided with the earth to supply this much water.

Assume that an average comet has a spherical nucleus 50 miles (80 kilometers) in radius. This corresponds to a volume

$$V(comet) = \frac{4}{3}\pi(8 \times 10^4\ \mathrm{m})^3 = 2 \times 10^{15}\ \mathrm{m}^3$$

The radius of the earth is roughly 6.4×10^6 m, so its surface area is

$$A = 4\pi(6.4 \times 10^6\ \mathrm{m})^2 = 5.1 \times 10^{14}\ \mathrm{m}^2$$

Roughly 70% of the earth's surface is covered by water. Assume an average depth of 1.0 kilometer for all bodies of water.

$$\begin{aligned} V(water) &= (0.70)(5.1 \times 10^{14}\ \mathrm{m}^2)(1000\ \mathrm{m}) \\ &= 3.6 \times 10^{17}\ \mathrm{m}^3 \end{aligned}$$

$$\text{Number of comets} \approx \frac{3.6 \times 10^{17}\ \mathrm{m}^3}{2 \times 10^{15}\ \mathrm{m}^3} \approx 200$$

Chapter 4

Vectors and Vector Algebra

EXERCISES

Exercise 4.1. Draw vector diagrams and convince yourself that the two schemes presented for the construction of $D = A - B$ give the same result.

Exercise 4.2. Find $\mathbf{A} - \mathbf{B}$ if $\mathbf{A} = (2.50, 1.50)$ and $\mathbf{B} = (1.00, -7.50)$

$$\mathbf{A} - \mathbf{B} = (1.50, 9.00) = 1.50\mathbf{i} + 9.00\mathbf{j}$$

Exercise 4.3. Let $|\mathbf{A}| = 4.00, |\mathbf{B}| = 2.00$, and let the angle between them equal 45.0°. Find $\mathbf{A} \cdot \mathbf{B}$.

$$\mathbf{A} \cdot \mathbf{B} = (4.00)(2.00)\cos(45°) = 8.00 \times 0.70711 = 5.66.$$

Exercise 4.4. If $\mathbf{A} = (3.00)\mathbf{i} - (4.00)\mathbf{j}$ and $\mathbf{B} = (1.00)\mathbf{i} + (2.00)\mathbf{j}$.

a. Draw a vector diagram of the two vectors.
b. Find $\mathbf{A} \cdot \mathbf{B}$ and $(2.00\mathbf{A}) \cdot (3.00\mathbf{B})$.

$$\begin{aligned} \mathbf{A} \cdot \mathbf{B} &= 3.00 \times 1.00 \\ &\quad +(-4.00)(2.00) = -5.00 \\ (2\mathbf{A}) \cdot (3\mathbf{B}) &= 6(-5.00) = -30.00 \end{aligned}$$

Exercise 4.5. If $\mathbf{A} = 2.00i - 3.00j$ and $\mathbf{B} = -1.00i + 4.00j$

a. Find $|\mathbf{A}|$ and $|\mathbf{B}|$.

$$\begin{aligned} |\mathbf{A}| &= A = \sqrt{4.00 + 9.00} = 3.606 \\ |\mathbf{B}| &= B = \sqrt{1.00 + 16.00} = 4.123 \end{aligned}$$

b. Find the components and the magnitude of $2.00\mathbf{A} - \mathbf{B}$.

$$\begin{aligned} 2.00\mathbf{A} - \mathbf{B} &= \mathbf{i}(4.00 + 1.00) + \mathbf{j}(-6.00 + 4.00) \\ &= \mathbf{i}(5.00) + \mathbf{j}(-2.00) \\ |2.00\mathbf{A} - \mathbf{B}| &= \sqrt{25.00 + 4.00} = 5.385 \end{aligned}$$

c. Find $\mathbf{A} \cdot \mathbf{B}$.

$$\mathbf{A} \cdot \mathbf{B} = (2.00)(-1.00) + (-3.00)(4.00) = -14.00$$

d. Find the angle between $\mathbf{A}$ and $\mathbf{B}$.

$$\begin{aligned} \cos(\alpha) &= \frac{\mathbf{A} \cdot \mathbf{B}}{AB} = \frac{-14.00}{(3.606)(4.123)} = -0.94176 \\ \alpha &= \arccos(-0.94176) = 2.799 \text{ rad} = 160.3° \end{aligned}$$

Exercise 4.6. Find the magnitude of the vector $\mathbf{A} = (-3.00, 4.00, -5.00)$.

$$A = \sqrt{9.00 + 16.00 + 25.00} = \sqrt{50.00} = 7.07$$

Exercise 4.7. **a.** Find the Cartesian components of the position vector whose spherical polar coordinates are $r = 2.00, \theta = 90°, \phi = 0°$. Call this vector $\mathbf{A}$.

$$\begin{aligned} x &= 2.00 \\ y &= 0.00 \\ z &= r\cos(\theta) = 0.00 \\ \mathbf{A} &= (2.00)\mathbf{i} \end{aligned}$$

b. Find the scalar product of the vector $\mathbf{A}$ from part a and the vector $\mathbf{B}$ whose Cartesian components are (1.00, 2.00, 3.00).

$$\mathbf{A} \cdot \mathbf{B} = 2.00 + 0 + 0 = 2.00$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00028-8

c. Find the angle between these two vectors. We must first find the magnitude of B.

$$\begin{aligned}|\mathbf{B}| &= B=\sqrt{1.00+4.00+9.00}\\ &=\sqrt{14.00}=3.742\\ \cos(\alpha) &= \frac{2.00}{(2.00)(3.742)}=0.26726\\ \alpha &= \arccos(0.26726)=74.5^\circ=1.300\text{ rad}\end{aligned}$$

Exercise 4.8. From the definition, show that

$$\boxed{\mathbf{A}\times\mathbf{B}=-(\mathbf{B}\times\mathbf{A})}.$$

This result follows immediately from the screw-thread rule or the right-hand rule, since reversing the order of the factors reverses the roles of the thumb and the index finger.

Exercise 4.9. Show that the vector **C** is perpendicular to **B**.

We do this by showing that $\mathbf{B}\cdot\mathbf{C}=0$.

$$\begin{aligned}\mathbf{B}\cdot\mathbf{C} &= B_xC_x+B_yC_y+B_zC_z\\ &= -1+2-1=0.\end{aligned}$$

Exercise 4.10. The magnitude of the earth's magnetic field ranges from 0.25 to 0.65 G (gauss). Assume that the average magnitude is equal to 0.45 G, which is equivalent to 0.000045 T. Find the magnitude of the force on the electron in the previous example due to the earth's magnetic field, assuming that the velocity is perpendicular to the magnetic field.

$$\begin{aligned}|\mathbf{F}|=F &= (1.602\times10^{-19}\text{ C})\\ &\quad\times(1.000\times10^{5}\text{ m s}^{-1})(0.000045\text{ T})\\ &= 7.210\times10^{-19}\text{ A s m s}^{-1}\text{ kg s}^{-2}\text{ A}^{-1}\\ &= 7.210\times10^{-19}\text{ kg m s}^{-2}=7.210\times10^{-19}\text{ N}\end{aligned}$$

Exercise 4.11. A boy is swinging a weight around his head on a rope. Assume that the weight has a mass of 0.650 kg, that the rope plus the effective length of the boy's arm has a length of 1.45 m and that the weight makes a complete circuit in 1.34 s. Find the magnitude of the angular momentum, excluding the mass of the rope and that of the boy's arm. If the mass is moving counterclockwise in a horizontal circle, what is the direction of the angular momentum?

$$\begin{aligned}v &= \frac{2\pi(1.45\text{ m})}{1.34\text{ s}}=6.80\text{ m s}^{-1}\\ L &= mvr=(0.650\text{ kg})(6.80\text{ m s}^{-1})\\ &\quad\times(1.45\text{ m})=6.41\text{ kg m}^2\text{ s}^{-1}\end{aligned}$$

By the right-hand rule, the angular momentum is vertically upward.

PROBLEMS

1. Find $\mathbf{A}-\mathbf{B}$ if $\mathbf{A}=2.00i+3.00j$ and $\mathbf{B}=1.00i+3.00j-1.00k$.

$$\mathbf{A}-\mathbf{B}=-1.00\mathbf{i}+2.00\mathbf{k}.$$

2. An object of mass $m=10.0$ kg near the surface of the earth has a horizontal force of 98.0 N acting on it in the eastward direction in addition to the gravitational force. Find the vector sum of the two forces (the resultant force). Let the gravitational force be denoted by W and the eastward force be denoted by $F=(98.0\text{ N})i$. Denote the resultant force by R.

$$\begin{aligned}\mathbf{R} &= \mathbf{F}+\mathbf{W}=(98.0\text{ N})\mathbf{i}-mg\mathbf{k}\\ &= (98.0\text{ N})\mathbf{i}-(10.0\text{ kg})(9.80\text{ m s}^{-2})\mathbf{k}\\ &= (98.0\text{ N})\mathbf{i}-(98.0\text{ kg m s}^{-2}\mathbf{k}\\ &= (98.0\text{ N})\mathbf{i}-(98.0\text{ N})\mathbf{k}\end{aligned}$$

The direction of this force is 45° from the vertical in the eastward direction.

3. Find $\mathbf{A}\cdot\mathbf{B}$ if $\mathbf{A}=(0,2)$ and $\mathbf{B}=(2,0)$.

$$\mathbf{A}\cdot\mathbf{B}=\mathbf{0}+\mathbf{0}=\mathbf{0}$$

4. Find $|\mathbf{A}|$ if $\mathbf{A}=3.00i+4.00j-5.00k$.

$$|\mathbf{A}|=\sqrt{9.00+16.00+25.00}=7.07$$

5. Find $\mathbf{A}\cdot\mathbf{B}$ if $A=(1.00)i+(2.00)j+(3.00)k$ and $B=(1.00)i+(3.00)j-(2.00)k$.

$$\mathbf{A}\cdot\mathbf{B}=1.00+6.00-6.00=1.00$$

6. Find $\mathbf{A}\cdot\mathbf{B}$ if $\mathbf{A}=(1.00,1.00,1.00)$ and $\mathbf{B}=(2.00,2.00,2.00)$.

$$\mathbf{A}\cdot\mathbf{B}=2.00+2.00+2.00=6.00$$

7. Find $\mathbf{A}\times\mathbf{B}$ if $\mathbf{A}=(0.00,1.00,2.00)$ and $\mathbf{B}=(2.00,1.00,0.00)$.

$$\begin{aligned}\mathbf{A}\times\mathbf{B} &= \mathbf{A}\times\mathbf{B}=\mathbf{i}(A_yB_z-A_zB_y)\\ &\quad+\mathbf{j}(A_zB_x-A_xB_z)+\mathbf{k}(A_xB_y-A_yB_x)\\ &= \mathbf{i}(0.00-2.00)+\mathbf{j}(4.00-0.00)\\ &\quad+\mathbf{k}(0.00-2.00)\\ &= -2.00\mathbf{i}+4.00\mathbf{j}-2.00\mathbf{k}\end{aligned}$$

8. Find $\mathbf{A}\times\mathbf{B}$ if $\mathbf{A}=(1,1,1)$ and $\mathbf{B}=(2,2,2)$.

$$\mathbf{A}\times\mathbf{B}=\mathbf{0}$$

9. Find the angle between **A** and **B** if $\mathbf{A} = 1.00i + 2.00j + 1.00k$ and $\mathbf{B} = 1.00i - 1.00k$.

$$\begin{aligned}\mathbf{A}\cdot\mathbf{B} &= 1.00 + 0 - 2.00 = -1.00\\ A &= \sqrt{1.00+4.00+1.00} = \sqrt{6.00} = 2.4495\\ B &= \sqrt{1.00+1.00} = \sqrt{2.00} = 1.4142\\ \cos(\alpha) &= \frac{-1.00}{(2.4495)(1.4142)} = -0.28868\\ \alpha &= \arccos(-0.28868) = 107^\circ = 1.86 \text{ rad}\end{aligned}$$

10. Find the angle between A and B if $A = 3.00i + 2.00j + 1.00k$ and $B = 1.00i + 2.00j + 3.00k$.

$$\begin{aligned}\mathbf{A}\cdot\mathbf{B} &= 3.00 + 4.00 + 3.00 = 10.00\\ A &= \sqrt{9.00+4.00+1.00} = \sqrt{14.00} = 3.7417\\ B &= \sqrt{1.00+4.00+9.00} = \sqrt{14.00} = 3.7417\\ \cos(\alpha) &= \frac{10.00}{(3.7417)(3.7417)} = 0.71429\\ \alpha &= \arccos(0.71429) = 44.4^\circ = 0.775 \text{ rad}\end{aligned}$$

11. A spherical object falling in a fluid has three forces acting on it: (1) The gravitational force, whose magnitude is $F_g = mg$, where m is the mass of the object and g is the acceleration due to gravity, equal to 9.80 m s^{-2}; (2) The buoyant force, whose magnitude is $F_b = m_f g$, where m_f is the mass of the displaced fluid, and whose direction is upward; (3) The frictional force, which is given by $F_f = -6\pi\eta r v$, where r is the radius of the object, v its velocity, and η the coefficient of viscosity of the fluid. This formula for the frictional forces applies only if the flow around the object is laminar (flow in layers). The object is falling at a constant speed in glycerol, which has a viscosity of $1490 \text{ kg m}^{-1}\text{ s}^{-1}$. The object has a mass of 0.00381 kg, has a radius of 0.00432 m, a mass of 0.00381 kg, and displaces a mass of fluid equal to 0.000337 kg. Find the speed of the object. Assume that the object has attained a steady speed, so that the net force vanishes.

$$\begin{aligned}F_{z,\text{total}} &= 0 = -(0.00381 \text{ kg})(9.80 \text{ m s}^{-2})\\ &\quad + (0.000337 \text{ kg})(9.80 \text{ m s}^{-2})\\ &\quad + 6\pi(1490 \text{ kg m}^{-1}\text{ s}^{-1})(0.00432 \text{ m})v\\ v &= \left|\frac{-(0.00381 \text{ kg})(9.80 \text{ m s}^{-2}) + (0.000337 \text{ kg})(9.80 \text{ m s}^{-2})}{6\pi(1490 \text{ kg m}^{-1}\text{ s}^{-1})(0.00432 \text{ m})}\right|\\ &= 0.18 \text{ m s}^{-1}\end{aligned}$$

12. An object has a force on it given by $\mathbf{F} = (4.75 \text{ N})i + (7.00 \text{ N})j + (3.50 \text{ N})k$.

a. Find the magnitude of the force.

$$\begin{aligned}F &= \sqrt{(4.75 \text{ N})^2 + (7.00 \text{ N})^2 + (3.50 \text{ N})^2}\\ &= \sqrt{83.8125} = 915 \text{ N}\end{aligned}$$

b. Find the projection of the force in the x-y plane. That is, find the vector in the x-y plane whose head is reached from the head of the force vector by moving in a direction perpendicular to the x-y plane.

$$\mathbf{F}_{\text{projection}} = (4.75 \text{ N})\mathbf{i} + (7.00 \text{ N})\mathbf{j}$$

13. An object of mass 12.000 kg is moving in the x direction. It has a gravitational force acting on it equal to $-mgk$, where m is the mass of the object and g is the acceleration due to gravity, equal to 9.80 m s^{-1}. There is a frictional force equal to $(0.240 \text{ N})i$. What is the magnitude and direction of the resultant force (the vector sum of the forces on the object)?

$$\begin{aligned}\mathbf{F}_{\text{total}} &= -(12.000 \text{ kg})(9.80 \text{ m s}^{-1})\mathbf{k} + (0.240 \text{ N})\mathbf{i}\\ &= -(117.60 \text{ N})\mathbf{k} + (0.240 \text{ N})\mathbf{i}\\ F_{\text{total}} &= \sqrt{(117.6 \text{ N})^2 + (0.240 \text{ N})^2} = 118 \text{ N}\end{aligned}$$

The angle between this vector and the negative z axis is

$$\alpha = \arctan\left(\frac{0.240}{117.6}\right) = 0.117^\circ = 0.00294 \text{ rad}$$

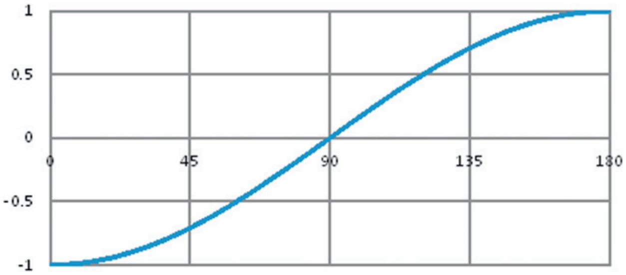
14. The potential energy of a magnetic dipole in a magnetic field is given by the scalar product

$$V = -\boldsymbol{\mu}\cdot\mathbf{B},$$

where B is the magnetic induction (magnetic field) and μ is the magnetic dipole. Make a graph of $\frac{V}{|\boldsymbol{\mu}||\mathbf{B}|}$ as a function of the angle between μ and B for values of the angle from 0° to 180°.

$$\frac{V}{|\boldsymbol{\mu}||\mathbf{B}|} = -\cos(\alpha)$$

Here is the graph



15. According to the Bohr theory of the hydrogen atom, the electron in the atom moves around the nucleus in one of various circular orbits with radius $r = a_0 n^2$ where a_0 is a distance equal to 0.529×10^{-10} m, called the Bohr radius and n is a positive integer. The mass of the electron is 9.109×10^{-31} kg. According to the theory, $L = nh/2\pi$, where h is Planck's constant, equal to 6.626×10^{-34} J s. Find the speed of the electron for $n = 1$ and for $n = 2$.

Since the orbit is circular, the position vector and the velocity are perpendicular to each other, and $L = mvr$.

For $n = 1$:

$$v = \frac{L}{mr} = \frac{(6.626 \times 10^{-34}\ \text{J s})}{2\pi(9.109 \times 10^{-31}\ \text{kg})(0.529 \times 10^{-10}\ \text{m})}$$
$$= 2.188 \times 10^{6}\ \text{m s}^{-1}$$

For $n = 2$

$$v = \frac{L}{mr} = \frac{2(6.626 \times 10^{-34}\ \text{Js})}{2\pi(9.109 \times 10^{-31}\ \text{kg})2^2(0.529 \times 10^{-10}\ \text{m})}$$
$$= 1.094 \times 10^{6}\ \text{m s}^{-1}$$

Notice that the speed for $n = 1$ is nearly 1% of the speed of light.

Chapter 5

Problem Solving and the Solution of Algebraic Equations

EXERCISES

Exercise 5.1. Show by substitution that the quadratic formula provides the roots to a quadratic equation.

For simplicity. we assume that $a = 1$.

$$\left(\frac{-b \pm \sqrt{b^2-4c}}{2}\right)^2 + b\left(\frac{-b \pm \sqrt{b^2-4c}}{2}\right) + c$$

$$= \frac{b^2}{4} \mp \frac{b\sqrt{b^2-4c}}{2} + \frac{b^2-4c}{4} - \frac{b^2}{4}$$

$$\pm \frac{b\sqrt{b^2-4c}}{2} + c = 0$$

Exercise 5.2. For hydrocyanic acid (HCN), $K_a = 4.9 \times 10^{-10}$ at 25 °C. Find $[H^+]$ if 0.1000 mol of hydrocyanic acid is dissolved in enough water to make 1.000 l. Assume that activity coefficients are equal to unity and neglect hydrogen ions from water.

$$x = \frac{-K_a \pm \sqrt{K_a^2 + 0.4000 K_a}}{2}$$

$$= \frac{-4.9 \times 10^{-10} \pm \sqrt{\left(4.9 \times 10^{-10}\right)^2 + (0.4000)\left(4.9 \times 10^{-10}\right)}}{2}$$

$$= 7.00 \times 10^{-6} \quad \text{or} \quad -7.00 \times 10^{-6}$$

$$[H^+] = [A^-] = 7.00 \times 10^{-6} \text{ mol l}^{-1}.$$

The neglect of hydrogen ions from water is acceptable, since neutral water provides 1×10^{-7} mol l^{-1} of hydrogen ions, and will provide even less in the presence of the acid.

Exercise 5.3. Carry out the algebraic manipulations to obtain the cubic equation in Eq. (5.9).

$$K_a = xy$$

$$y = \frac{K_a}{x}$$

where we let $y = [A^-]/c^\circ$. Since the ionization of water and the ionization of the acid both produce hydrogen ions,

$$\frac{[HA]}{c^\circ} = \frac{c}{c^\circ} - (x - y)$$

$$K_a = \frac{x\left[x - \dfrac{K_w}{x}\right]}{\dfrac{c}{c^\circ} - x + \dfrac{K_w}{x}}$$

$$K_a\left[\frac{c}{c^\circ} - x + \frac{K_w}{x}\right] = x^2 - K_w$$

Multiply this equation by x and collect the terms:

$$x^3 + K_a x^2 - \left(\frac{cK_a}{c^\circ} + K_w\right)x - K_a K_w = 0$$

Exercise 5.4. Solve for the hydrogen ion concentration in a solution of acetic acid with stoichiometric molarity equal to 0.00100 mol l^{-1}. Use the method of successive approximations.

For the first approximation

$$x^2 = \left(1.754 \times 10^{-5}\right)(0.00100 - x)$$

$$\approx (1.754 \times 10^{-5})(0.00100) = 1.754 \times 10^{-8}$$

$$x \approx \sqrt{1.754 \times 10^{-8}} = 1.324 \times 10^{-4}$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00029-X

For the next approximation

$$\begin{aligned}
x^2 &= \left(1.754 \times 10^{-5}\right)(0.00100 - 1.324 \times 10^{-4}) \\
&\approx \left(1.754 \times 10^{-5}\right)(8.676 \times 10^{-4}) \\
&= 1.5217 \times 10^{-8} \\
x &\approx \sqrt{1.5217 \times 10^{-8}} = 1.236 \times 10^{-4}
\end{aligned}$$

For the third approximation

$$\begin{aligned}
x^2 &= (1.754 \times 10^{-5})(0.00100 - 1.236 \times 10^{-4}) \\
&\approx (1.754 \times 10^{-5})(8.7664 \times 10^{-4}) \\
&= 1.5376 \times 10^{-8} \\
x &\approx \sqrt{1.5376 \times 10^{-8}} = 1.24 \times 10^{-4} \\
[\mathrm{H}^+] &= 1.24 \times 10^{-4}\ \mathrm{mol\ l^{-1}}
\end{aligned}$$

Since the second and third approximations yielded nearly the same answer, we stop at this point.

Exercise 5.5. Verify the prediction of the ideal gas equation of state given in the previous example.

$$\begin{aligned}
V_\mathrm{m} &= \frac{V}{n} = \frac{RT}{P} \\
&= \frac{\left(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)(298.15\ \mathrm{K})}{1.01325 \times 10^6\ \mathrm{Pa}} \\
&= 2.447 \times 10^{-3}\ \mathrm{m^3\ mol^{-1}}
\end{aligned}$$

Exercise 5.6. Substitute the value of the molar volume obtained in the previous example and the given temperature into the Dieterici equation of state to calculate the pressure. Compare the calculated pressure with 10.00 atm $= 1.01325 \times 10^6$ Pa, to check the validity of the linearization approximation used in the example.

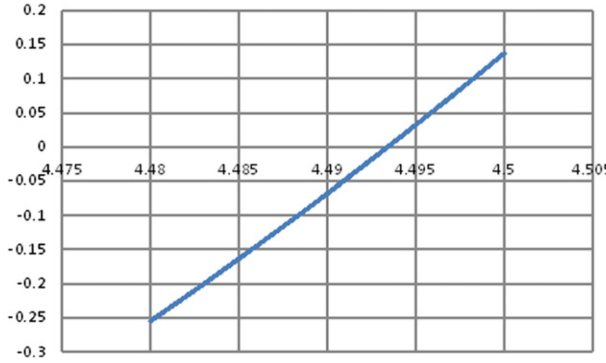
$$\begin{aligned}
Pe^{a/V_\mathrm{m}RT}(V_\mathrm{m} - b) &= RT \\
P &= \frac{RTe^{-a/V_\mathrm{m}RT}}{(V_\mathrm{m} - b)} \\
e^{-a/V_\mathrm{m}RT} &= \exp\left[-\frac{\left(0.468\ \mathrm{Pa\ m^6\ mol^{-2}}\right)}{\left(2.30 \times 10^{-3}\ \mathrm{m^3\ mol^{-1}}\right)\left(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)(298.15\ \mathrm{K})}\right] \\
&= e^{-8.208 \times 10^{-2}} = 0.9212 \\
P &= \frac{RTe^{-a/V_\mathrm{m}RT}}{(V_\mathrm{m} - b)} \\
&= \frac{\left(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)(298.15\ \mathrm{K})(0.9212)}{\left(2.30 \times 10^{-3}\ \mathrm{m^3\ mol^{-1}} - 4.63 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}\right)} \\
&= 1.013328 \times 10^6\ \mathrm{Pa}
\end{aligned}$$

which compares with 1.01325×10^6 Pa.

Exercise 5.7. Find approximately the smallest positive root of the equation

$$\tan(x) - x = 0.$$

Since $\tan(x)$ is larger than x in the entire range from $x = 0$ to $x = \pi$, we look at the range from $x = \pi$ to $x = 2\pi$. By trial and error we find that the root is near 4.49. The following graph of $\tan(x) - x$ shows that the root is near $x = 4.491$.

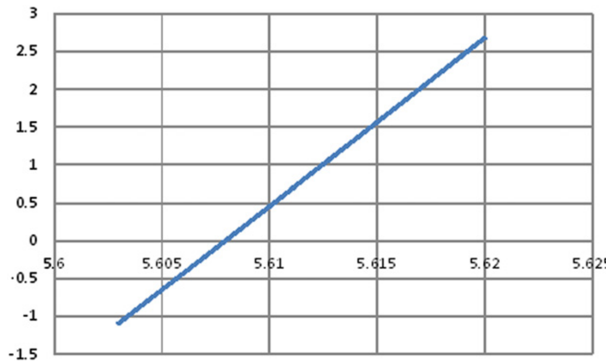


Exercise 5.8. Using a graphical procedure, find the most positive real root of the quartic equation:

$$x^4 - 4.500x^3 - 3.800x^2 - 17.100x + 20.000 = 0$$

The curve representing this function crosses the x axis in only two places. This indicates that two of the four roots are complex numbers. Chemists are not usually interested in complex roots to equations.

A preliminary graph indicates a root near $x = 0.9$ and one near $x = 5.5$. The following graph indicates that the root is near $x = 5.608$. To five significant digits, the correct answer is $x = 5.6079$.



Exercise 5.9. Use the method of trial and error to find the two positive roots of the equation

$$e^x - 3.000x = 0$$

to five significant digits. Begin by making a graph of the function to find the approximate locations of the roots.

A rough graph indicates a root near $x = 0.6$ and a root $x = 1.5$. By trial and error, values of 0.61906 and 1.5123 were found.

Exercise 5.10. Use Excel to find the real root of the equation

$$x^3 + 5.000x - 42.00 = 0$$

The result is that $x = 3.9529$.

Exercise 5.11. Write Mathematica expressions for the following:

a. The complex conjugate of $(10)e^{2.657i}$

10 Exp[−2.635 I]

b. $\ln(100!) - (100\ln(100) - 100)$

Log[100!] − (100 Log[100] − 100]

c. The complex conjugate of $(1 + 2i)^{2.5}$

(1+2I)^2.5

Exercise 5.12. In the study of the rate of the chemical reaction:

$$a\mathrm{A} + b\mathrm{B} \rightarrow \text{products}$$

the quotient occurs:

$$\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)}$$

where $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$ are the initial concentrations of A and B, a and b are the stoichiometric coefficients of these reactants, and x is a variable specifying the extent to which the reaction has occurred. Write a Mathematica statement to decompose the denominator into partial fractions.

In[1] := **Clear**[*x*]
Apart [1/ ((A − a*x) (B − b*x))]

Exercise 5.13. Verify the real solutions in the preceding example by substituting them into the equation.

The equation is

$$f(x) = x^4 - 5x^3 + 4x^2 - 3x + 2 = 0$$

By calculation

$$f(0.802307) = 8.3 \times 10^{-7}$$
$$f(4.18885) = 0.000182$$

By trial and error, these roots are correct to the number of significant digits given.

Exercise 5.14. Use the *NSolve* statement in Mathematica to find the numerical values of the roots of the equation

$$x^3 + 5.000x - 42.00 = 0$$

The result is

$$x = \begin{cases} 3.00 \\ -1.500 + 3.4278i \\ -1.500 - 3.4278i \end{cases}$$

Use the *Find Root* statement to find the real root of the same equation.
The result is

$$x = 3.00$$

Exercise 5.15. Solve the simultaneous equations by the method of substitution:

$$\begin{aligned} x^2 - 2xy - x &= 0 \\ x + y &= 0 \end{aligned}$$

We replace y in the first equation by $-x$:

$$x^2 + 2x^2 - x = 3x^2 - x = 0$$

This equation can be factored

$$x(3x - 1) = 0$$

This has the two solutions:

$$x = \begin{cases} 0 \\ \frac{1}{3} \end{cases}$$

The first solution set is

$$x = 0, \quad y = 0$$

The second solution set is

$$x = \frac{1}{3}, \quad y = -\frac{1}{3}$$

Exercise 5.16. Solve the set of equations

$$\begin{aligned} 3x + 2y &= 40 \\ 2x - y &= 10 \end{aligned}$$

We multiply the second equation by 2 and add it to the first equation

$$\begin{aligned} 7x &= 60 \\ x &= \frac{60}{7} \end{aligned}$$

We substitute this into the second equation

$$\frac{120}{7} - y = 10$$
$$y = \frac{120}{7} - 10 = \frac{50}{7}$$

Substitute these values into the second equation to check our work;

$$\frac{120}{7} - \frac{50}{7} = \frac{70}{7} = 10$$

Exercise 5.17. Determine whether the set of equations has a nontrivial solution, and find the solution if it exists:

$$\begin{aligned} 5x + 12y &= 0 \\ 15x + 36y &= 0. \end{aligned}$$

We multiply the first equation by 3, which makes it identical with the second equation. There is a nontrivial solution that gives y as a function of x. From the first equation

$$y = -\frac{5x}{12} = -0.4167x$$

Exercise 5.18. Use Mathematica to solve the simultaneous equations

$$\begin{aligned} 2x + 3y &= 13 \\ x - 4y &= -10 \end{aligned}$$

The result is

$$\begin{aligned} x &= 2 \\ y &= 3 \end{aligned}$$

PROBLEMS

1. Solve the quadratic equations:

a.

$$\begin{aligned} x^2 - 3x + 2 &= 0 \\ (x-2)(x-1) &= 0 \\ x &= \begin{cases} 1 \\ 2 \end{cases} \end{aligned}$$

b.

$$\begin{aligned} x^2 - 1 &= 0 \\ (x-1)(x+1) &= 0 \end{aligned}$$

$$x = \begin{cases} 1 \\ -1 \end{cases}$$

c.

$$\begin{aligned} x^2 + x + 2 &= 0 \\ x &= \frac{-1 \pm \sqrt{1-8}}{2} = -\frac{1}{2} \pm \frac{\sqrt{7}i}{2} \\ &= 0.500 \pm 1.323i \end{aligned}$$

2. Solve the following equations by factoring:

a.

$$x^3 + x^2 - x - 1 = 0$$

By carrying out a long division, we find that $x - 1$ is a factor and the other factor is $x^2 + 2x + 1$, so that the factors are

$$x^3 + x^2 - x - 1 = (x-1)(x+1)^2$$

The roots are

$$x = \begin{cases} 1 \\ -1 \\ -1 \end{cases}$$

b.

$$x^4 - 1 = 0$$

This is factored as follows:

$$\begin{aligned} x^4 - 1 &= (x^2 + 1)(x^2 - 1) \\ &= (x+i)(x-i)(x+1)(x-1) \end{aligned}$$

The roots are

$$x = -i, i, -1, 1$$

3. Rewrite the factored quadratic equation $(x - x_1)(x - x_2) = 0$ in the form $x^2 - (x_1 + x_2)x + x_1x_2 = 0$. Apply the quadratic formula to this version and show that the roots are $x = x_1$ and $x = x_2$.

$$\begin{aligned} x &= \frac{x_1 + x_2 \pm \sqrt{(x_1+x_2)^2 - 4x_1x_2}}{2} \\ &= \frac{x_1 + x_2 \pm \sqrt{x_1^2 + 2x_{12}x + x_2^2 - 4x_1x_2}}{2} \\ &= \frac{x_1 + x_2 \pm \sqrt{x_1^2 - 2x_{12}x + x_2^2}}{2} \\ &= \frac{x_1 + x_2 \pm (x_1 - x_2)}{2} = \begin{cases} x_1 \text{ if } + \text{ is chosen} \\ x_2 \text{ if } - \text{ is chosen} \end{cases} \end{aligned}$$

4. The pH is defined for our present purposes as

$$\text{pH} = -\log_{10}([\text{H}^+]c^\circ)$$

Find the pH of a solution formed from 0.0500 mol of NH_3 and enough water to make 1.000 l of solution. The ionization that occurs is

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

The equilibrium expression in terms of molar concentrations is

$$K_b = \frac{([NH_4^+]c°)([OH^-]/c°)}{x(H_2O)([NH_3]c°)} \approx \frac{([NH_4^+]/c°)([OH^-]/c°)}{([NH_3]/c°)}$$

where $x(H_2O)$ represents the mole fraction of water, which is customarily used instead of its molar concentration. Since the mole fraction of the solvent in a dilute solution is nearly equal to unity, we can use the approximate version of the equation. The base ionization constant of NH_3, denoted by K_b, equals 1.80×10^{-5} at 25 °C.

$$1.80 \times 10^{-5} = \frac{x^2}{0.0500 - x}$$

where we assume that OH^- ions from water can be neglected and where we let $x = ([NH_4^+]/c°) = ([OH^-]/c°)$

$$\begin{aligned} x^2 &= (1.80 \times 10^{-5})(0.0500 - x) \\ x^2 &\approx (1.80 \times 10^{-5})(0.0500) = 9.00 \times 10^{=7} \\ x &\approx 9.49 \times 10^{-4} \\ x^2 &\approx \left(1.80 \times 10^{-5}\right)\left(0.0500 - 9.49 \times 10^{-4}\right) \\ &= 8.83 \times 10^{=7} \\ x &\approx 9.40 \times 10^{-4} \end{aligned}$$

We stop the iteration at this point.

$$\begin{aligned} \text{pOH} &= -\log\left(9.40 \times 10^{-4}\right) = 3.03 \\ \text{pH} &= 14.00 - 3.03 = 10.97 \end{aligned}$$

5. The acid ionization constant of chloroacetic acid is equal to 1.40×10^{-3} at 25 °C. Assume that activity coefficients are equal to unity and find the hydrogen ion concentration at the following stoichiometric molarities.

a. 0.100 mol l^{-1}

$$\begin{aligned} 1.40 \times 10^{-3} &= \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} \\ x &\approx \left[\left(1.40 \times 10^{-3}\right)(0.100)\right]^{1/2} \\ &= 0.0118 \\ x &\approx \left[\left(1.40 \times 10^{-3}\right)(0.100 - 0.0118)\right]^{1/2} \\ &= 0.0111 \\ x &\approx \left[\left(1.40 \times 10^{-3}\right)(0.100 - 0.0111)\right]^{1/2} \\ &= 0.0112 \\ [H^+] &= 0.011 \text{ mol } l^{-1} \end{aligned}$$

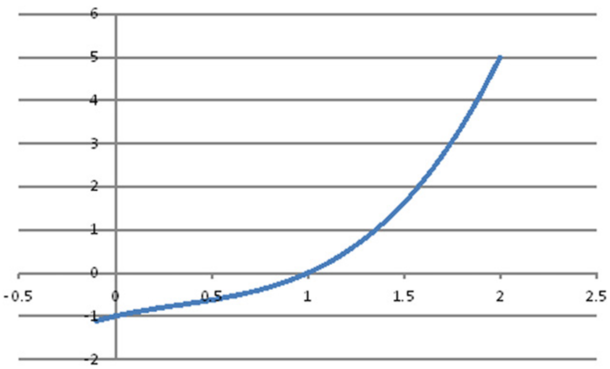
b. 0.0100 mol l^{-1}

$$\begin{aligned} 1.40 \times 10^{-3} &= \frac{x^2}{0.0100 - x} \approx \frac{x^2}{0.0100} \\ x &\approx [(1.40 \times 10^{-3})(0.0100)]^{1/2} \\ &= 0.00374 \\ x &\approx [(1.40 \times 10^{-3})(0.0100 - 0.00374)]^{1/2} \\ &= 0.00296 \\ x &\approx [(1.40 \times 10^{-3})(0.0100 - 0.00296)]^{1/2} \\ &= 0.00314 \\ x &\approx [(1.40 \times 10^{-3})(0.0100 - 0.00314)]^{1/2} \\ &= 0.00310 \\ [H^+] &= 0.0031 \text{ mol } l^{-1} \end{aligned}$$

6. Find the real roots of the following equations by graphing:

a.

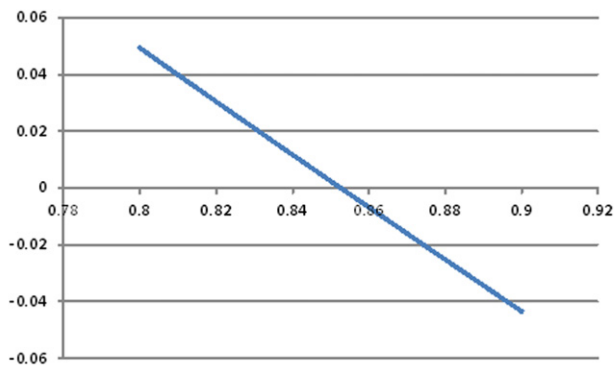
$$x^3 - x^2 + x - 1 = 0$$



The only real root is $x = 1$.

b.

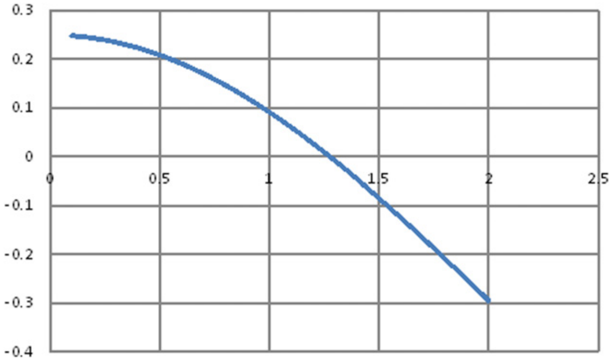
$$e^{-x} - 0.500x = 0$$



To four digits, the root is $x = 0.8527$.

c.

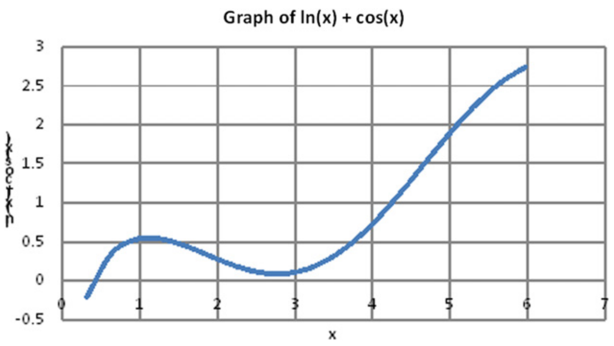
$$\sin(x)/x - 0.75 = 0.$$



To four digits, the root is at $x = 1.2755$

7. Make a properly labeled graph of the function $y(x) = \ln(x) + \cos(x)$ for values of x from 0 to 2π

a.



b. Repeat part a using Mathematica.

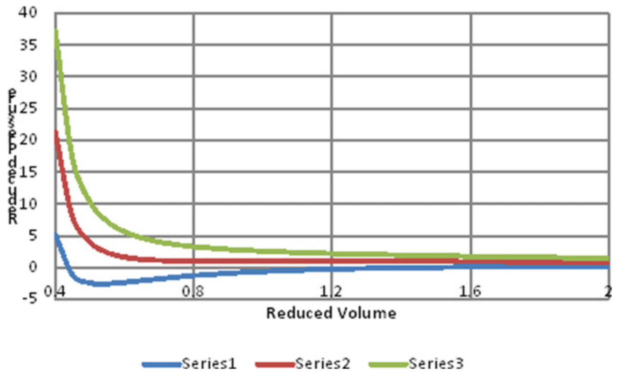
8. When expressed in terms of "reduced variables" the van der Waals equation of state is

$$\left(P_\mathrm{r} + \frac{3}{V_\mathrm{r}^2}\right)\left(V_\mathrm{r} - \frac{1}{3}\right) = \frac{8T_r}{3}$$

$$P_\mathrm{r} = \frac{8T_r}{3\left(V_\mathrm{r} - \frac{1}{3}\right)} - \frac{3}{V_\mathrm{r}^2}$$

a. Using Excel, construct a graph containing three curves of P_r as a function of V_r: for the range $0.4 < V_\mathrm{r} < 2$: one for $T_r = 0.6$, one for $T_r = 1$, and one for $T_r = 1.4$.

In this graph, Series 1 represents $T_r = 0.6$, Series 2 represents $T_r = 1$, and Series 3 represents $T_r = 1.4$.

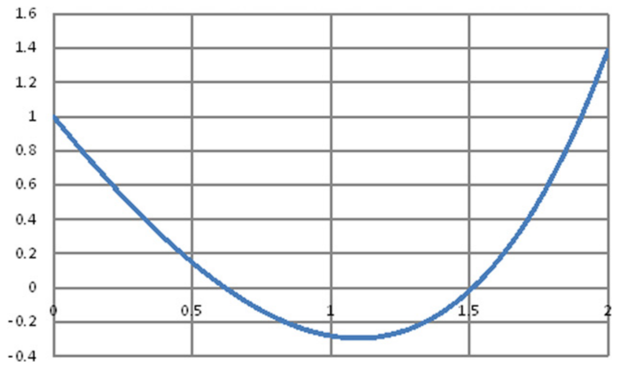


b. Repeat part a using Mathematica.

9. Using a graphical method, find the two positive roots of the following equation.

$$e^x - 3.000x = 0.$$

The following graph indicates a root near $x = 0.6$ and one near $x = 1.5$.

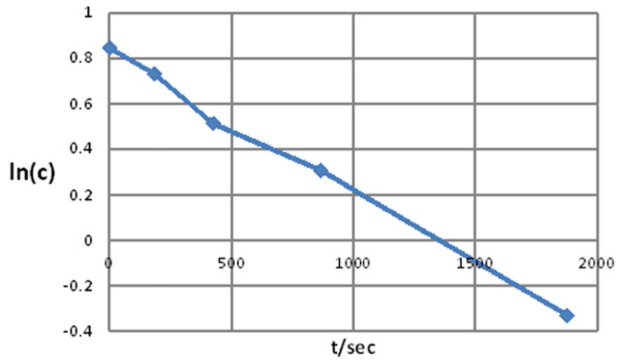


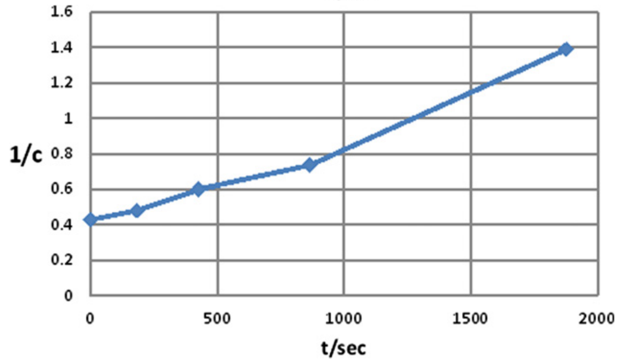
By trial and error, the roots are at $x = 0.61906$ and $x = 1.5123$

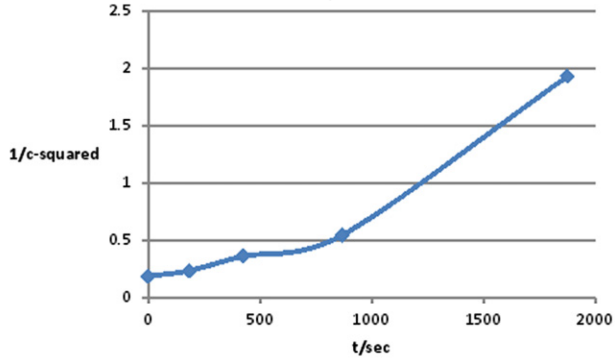
10. The following data were taken for the thermal decomposition of N_2O_3:

t/s	0	184	426	867	1877
$[N_2O_3]$/mol l^{-1}	2.33	2.08	1.67	1.36	0.72

Using Excel, make three graphs: one with $\ln([N_2O_3])$ as a function of t, one with $1/[N_2O_3]$ as a function of t, and one with $1/[N_2O_3]^2$ as a function of t. Determine which graph is most nearly linear. If the first graph is most nearly linear, the reaction is first order; if the second graph is most nearly linear, the reaction is second order, and if the third graph is most nearly linear, the reaction is third order.







Because of experimental error, it is a little difficult to tell, but it appears that the plot of $\ln(c)$ is more nearly linear, so the reaction is apparently first order.

11. Write an Excel worksheet that will convert a list of distance measurements in meters to miles, feet, and inches. If the length in meters is typed into a cell in column A, let the corresponding length in miles appear on the same line in column B, the length in feet in column C, and the length in inches in column C. Here is the result:

meters	miles	feet	inches
1	0.000621371	3.28084	39.37007874
2	0.001242742	6.56168	78.74015748
5	0.003106855	16.4042	196.8503937
10	00.00621371	32.8084	393.7007874
100	0.0621371	328.084	3937.007874

12. The van der Waals equation of state is

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

where a and b are temperature-independent parameters that have different values for each gas. For carbon dioxide

$$\begin{aligned} a &= 0.3640 \text{ Pa m}^6 \text{ mol}^{-2} \\ b &= 4.267 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

a. Write the van der Waals equation of state as a cubic equation in V.

$$PV + \frac{n^2 a}{V} - Pnb - \frac{n^3 ab}{V^2} = nRT$$

Multiply by V^2:

$$\begin{aligned} PV^3 + n^2 aV - PnbV^2 - n^3 ab &= nRTV^2 \\ PV^3 - (Pnb + nRT)\,V^2 + n^2 aV - n^3 ab &= 0 \end{aligned}$$

b. Use the NSolve statement in Mathematica to find the volume of 1.000 mol of carbon dioxide at $P = 1.000$ bar (100000 Pa) and $T = 298.15$ K. Notice that two of the three roots are complex, and must be ignored. Compare your result with the prediction of the ideal gas equation of state.

$$\begin{aligned} &(100000\text{ Pa})V^3 \\ &-\Big[(100000\text{ Pa})(4.267 \times 10^{-5}\text{ m}^3) \\ &+ (8.3145\text{ J K}^{-1})(298.15\text{ K})\Big]V^2 \\ &+ (0.3640\text{ Pa m}^6)V \\ &- (0.3640\text{ Pa m}^6)(4.267 \times 10^{-5}\text{ m}^3) = 0 \end{aligned}$$

All terms have the same units, so temporarily omit the units and divide by 100000.

$$\begin{aligned} &V^3 - 0.02483V^2 + .00000364V \\ &\qquad -1.55 \times 10^{-10} = 0 \\ &V = 2.4683 \times 10^{-2}\text{ m}^3 \end{aligned}$$

From the ideal gas equation

$$\begin{aligned} V &- \frac{nRT}{P} \\ &= \frac{(1.000\text{ mol})(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K})}{100000\text{ Pa}} \\ &= 2.789 \times 10^{-2}\text{ m}^3 \end{aligned}$$

c. Use the Find Root statement in Mathematica to find the real root in part b. The result is:

$$V = 2.4683 \times 10^{-2}\text{ m}^3$$

d. Repeat part b for $P = 10.000$ bar (1.0000×10^6 Pa) and $T = 298.15$ K. Compare your result with the prediction of the ideal gas equation of state.

$$
\begin{aligned}
&(1000000\ \text{Pa})V^3 \\
&\quad - [(1000000\ \text{Pa})(4.267 \times 10^{-5}\ \text{m}^3) \\
&\quad + (8.3145\ \text{J K}^{-1})(298.15\ \text{K})]V^2 \\
&\quad + (0.3640\ \text{Pa m}^6)V - (0.3640\ \text{Pa m}^6) \\
&\quad \times (4.267 \times 10^{-5}\ \text{m}^3) = 0
\end{aligned}
$$

All terms have the same units, so temporarily omit the units and divide by 1000000.

$$
\begin{aligned}
&V^3 - 0.0025216V^2 + .000000364V \\
&\quad -1.55 \times 10^{-11} = 0
\end{aligned}
$$

The real root is

$$V = 2.3708 \times 10^{-3}\ \text{m}^3$$

From the ideal gas equation

$$
\begin{aligned}
V - \frac{nRT}{P} \\
&= \frac{(1.000\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}{1000000\ \text{Pa}} \\
&= 2.789 \times 10^{-3}\ \text{m}^3
\end{aligned}
$$

13. An approximate equation for the ionization of a weak acid, including consideration of the hydrogen ions from water is

$$[\text{H}^+]/c^\text{o} = \sqrt{K_\text{a}c/c^\text{o} + K_\text{w}},$$

where c is the gross acid concentration. This equation is based on the assumption that the concentration of unionized acid is approximately equal to the gross acid concentration. Consider a solution of HCN (hydrocyanic acid) with stoichiometric acid concentration equal to 1.00×10^{-5} mol l^{-1}. $K_\text{a} = 4.0 \times 10^{-10}$ for HCN. At this temperature, $K_\text{w} = 1.00 \times 10^{-14}$.

a. Calculate $[\text{H}^+]$ using this equation.

$$
\begin{aligned}
&[\text{H}^+]/c^\text{o} \\
&\quad = \sqrt{(4.0 \times 10^{-10})(1.00 \times 10^{-5}) + 1.00 \times 10^{-14}} \\
&\quad = 1.18 \times 10^{-7} \approx 1.2 \times 10^{-7}
\end{aligned}
$$

Roughly 20% greater than the value in pure water.

b. Calculate $[\text{H}^+]/c^\text{o}$ using Eq. (5.9).

$$
\begin{aligned}
&x^3 + \left(4.0 \times 10^{-10}\right)x^2 \\
&\quad - \left[\left(1.00 \times 10^{-5}\right)\left(4.0 \times 10^{-10}\right) + 1.00 \right. \\
&\quad \left. \times 10^{-14}\right]x - \left(4.0 \times 10^{-10}\right)\left(1.00 \times 10^{-14}\right) = 0 \\
&x^3 + \left(4.0 \times 10^{-15}\right)x^2 \\
&\quad - \left(1.00 \times 10^{-14}\right)x - 4.0 \times 10^{-25} = 0
\end{aligned}
$$

The solution is

$$
x = \begin{cases} -4.0 \times 10^{-11} \\ -9.9980 \times 10^{-8} \\ 1.0002 \times 10^{-7} \end{cases}
$$

We reject the negative roots and take $[\text{H}^+]/c^\text{o} = 1.0002 \times 10^{-7}$, barely more than the value in pure water.

14. Find the smallest positive root of the equation.

$$\sinh(x) - x^2 - x = 0.$$

A graph indicates a root near $x = 3.4$. By trial and error, the root is found at $x = 3.9925$.

15. Solve the cubic equation by trial and error, factoring, or by using Mathematica or Excel:

$$x^3 + x^2 - 4x - 4 = 0$$

This equation can be factored:

$$(x + 1)(x - 2)(x + 2) = 0$$

The solution is:

$$
x = \begin{cases} -2 \\ -1 \\ 2 \end{cases}
$$

16. Find the real root of the equation

$$x^2 - e^{-x} = 0$$

The solution is:

$$x = 0.70347$$

17. Find the root of the equation

$$x - 2.00\sin(x) = 0$$

By trial and error, the solution is

$$x = 1.8955$$

18. Find two positive roots of the equation

$$\ln(x) - 0.200x = 0$$

A graph indicates roots near $x = 1.3$ and $x = 13$. The roots are

$$x = \begin{cases} 1.2959 \\ 12.713 \end{cases}$$

19. Find the real roots of the equation

$$x^2 - 2.00 - \cos(x) = 0$$

A graph indicates roots near $x = \pm 1.4$. By trial and error, the roots are

$$x = \pm 1.4546$$

20. In the theory of blackbody radiation, the following equation

$$x = 5(1 - e^{-x})$$

needs to be solved to find the wavelength of maximum spectral radiant emittance. The variable x is

$$x = \frac{hc}{\lambda_{max} k_B T}$$

where λ_{max} is the wavelength of maximum spectral radiant emittance, h is Planck's constant, c is the speed of light, k_B is Boltzmann's constant, and T is the absolute temperature. Solve the equation numerically for a value of x. Find the value of λ_{max} for $T = 5800$ K. In what region of the electromagnetic spectrum does this value lie?

A graph indicates a root near $x = 4.96$. By trial and error, the solution is

$$x = 4.965$$

$$\begin{aligned} \lambda_{max} &= \frac{hc}{x k_B T} \\ &= \frac{(6.6260755 \times 10^{-34}\ \mathrm{J\ s})(2.99792458 \times 10^{8}\ \mathrm{m\ s^{-1}})}{(4.965)(1.3806568 \times 10^{-23}\mathrm{J\ K^{-1}})(5800\ \mathrm{K})} \\ &= 4.996 \times 10^{-7}\ \mathrm{m} = 499.6\ \mathrm{nm} \end{aligned}$$

This lies in the blue-green region of the visible spectrum.

21. Solve the simultaneous equations by hand, using the method of substitution:

$$\begin{aligned} x^2 + x + 3y &= 15 \\ 3x + 4y &= 18 \end{aligned}$$

Use Mathematica to check your result. Since the first equation is a quadratic equation, there will be two solution sets.

$$y = \frac{18 - 3x}{4}$$

Substitute this into the first equation

$$\begin{aligned} x^2 + x + 3\left(\frac{18 - 3x}{4}\right) &= 15 \\ x^2 + \left(1 - \frac{9}{4}\right)x + \frac{54}{4} &= 15 \\ x^2 - 1.25x + 13.5 &= 15 \\ x^2 - 1.25x - 1.50 &= 0 \\ 4x^2 - 5x - 6 &= 0 \\ x &= \frac{5 \pm \sqrt{25 + 96}}{8} \\ &= \frac{5 \pm \sqrt{121}}{8} \\ x &= \frac{5 \pm 11}{8} = \begin{cases} 2 \\ -\dfrac{3}{4} \end{cases} \end{aligned}$$

Check the $x = -3/4$ value:

$$4\left(\frac{9}{16}\right) - 5\left(\frac{3}{4}\right) - 6 =$$

For $x = 2$

$$y = \frac{18 - 6}{4} = 3$$

For $x = -3/4$

$$y = \frac{18 + 9/4}{4} = \frac{18 + 2.25}{4} = 5.0625$$

Check this

$$\frac{9}{16} - \frac{3}{4} + 3(5.0625) = 15$$

22. Stirling's approximation for $\ln(N!)$ is

$$\ln(N!) \approx \frac{1}{2}\ln(2\pi N) + N\ln(N) - N$$

Determine the validity of this approximation and of the less accurate version

$$\ln(N!) \approx N\ln(N) - N$$

for several values of N up to $N = 100$. Use a calculator, Excel, or Mathematica. Here are a few values

N	$\ln(N!)$	$\frac{1}{2}\ln(2\pi N) + N\ln(N) - N$	$N\ln(N) - N$
5	4.787491743	4.770847051	3.047189562
10	15.10441257	15.09608201	13.02585093
50	148.477767	148.4761003	145.6011503
100	363.7393756	363.7385422	360.5170186

23. The Dieterici equation of state is

$$Pe^{a/V_{\mathrm{m}}RT}(V_{\mathrm{m}}-b)=RT,$$

where P is the pressure, T is the temperature, V_{m} is the molar volume, and R is the ideal gas constant. The constant parameters a and b have different values for different gases. For carbon dioxide, $a = 0.468\ \mathrm{Pa\ m^6\ mol^{-2}}$, $b = 4.63\times10^{-5}\ \mathrm{m^3\ mol^{-1}}$. Without linearization, find the molar volume of carbon dioxide if $T = 298.15$ K and $P = 10.000\ \mathrm{atm} = 1.01325\times10^6$ Pa. Use Mathematica, Excel, or trial and error.

$$\begin{aligned}&(1.01325\times10^6\ \mathrm{Pa})\\&\quad\exp\left(\frac{0.468\ \mathrm{Pa\ m^6\ mol^{-2}}}{V_{\mathrm{m}}(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\right)\\&\quad\times(V_{\mathrm{m}}-4.63\times10^{-5}\ \mathrm{m^3\ mol^{-1}})\\&\quad=(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})\end{aligned}$$

Divide this equation by $(1.01325\times10^6\ \mathrm{Pa})$ and ignore the units

$$\begin{aligned}&\exp\left(\frac{0.468\ \mathrm{Pa\ m^6\ mol^{-2}}}{V_{\mathrm{m}}(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K}}\right)\\&\quad\times(V_{\mathrm{m}}-4.63\times10^{-5}\ \mathrm{m^3\ mol^{-1}})\\&\quad=\frac{(8.3145\mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}{(1.01325\times10^6\ \mathrm{Pa})}\\&\exp\left(\frac{0.00018879}{V_{\mathrm{m}}}\right)(V_{\mathrm{m}}-4.63\times10^{-5})-0.00244655=0\end{aligned}$$

Using trial and error with various values of V_{m} we seek a value so that this quantity vanishes. The result was

$$V_{\mathrm{m}}=0.0023001\ \mathrm{m^3\ mol^{-1}}$$

Compare this with the ideal gas value:

$$\begin{aligned}V_{\mathrm{m}}&=\frac{RT}{P}=\frac{(8.3145\mathrm{J\ K^{-1}mol^{-1}})(298.15\ \mathrm{K})}{(1.01325\times10^6\ \mathrm{Pa})}\\&=0.002447\ \mathrm{m^3\ mol^{-1}}\end{aligned}$$

24. Determine which, if any, of the following sets of equations are inconsistent or linearly dependent. Draw a graph for each set of equations, showing both equations. Find the solution for any set that has a unique solution.

a.

$$\begin{aligned}x+3y&=4\\2x+6y&=8\end{aligned}$$

These equations are linearly dependent, since the second equation is equal to twice the first equation

b.

$$\begin{aligned}3x_1+4x_2&=10\\4x_1-2x_2&=6\end{aligned}$$

Try the method of substitution. From the second equation

$$x=8-2y$$

Substitute this into the first equation

$$\begin{aligned}2(8-2y)+4y&=24\\0&=8\end{aligned}$$

The equations are inconsistent

c.

$$\begin{aligned}3x_1+4x_2&=10\\4x_1-2x_2&=6\end{aligned}$$

Solve the second equation for x_2 and substitute the result into the first equation:

$$\begin{aligned}x_2&=2x_1-3\\3x_1+4\left(2x_1-3\right)&=10\\11x_1&=22\\x_1&=2\\6+4x_2&=10\\x_2&=1\end{aligned}$$

25. Solve the set of equations using Mathematica or by hand with the method of substitution:

$$\begin{aligned}x^2-2xy+y^2&=0\\2x+3y&=5\end{aligned}$$

To solve by hand we first solve the quadratic equation for y in terms of x. The equation can be factored into two identical factors:

$$x^2-2xy+y^2=\left(x-y\right)^2=0$$

Both roots of the equation are equal:

$$y=x$$

We substitute this into the second equation

$$\begin{aligned}2x+3y&=5x=5\\x&=1\end{aligned}$$

The final solution is

$$\begin{aligned}x&=1\\y&=1\end{aligned}$$

Since the two roots of the quadratic equal were equal to each other, this is the only solution.

Alternate solution: Solve the second equation for y

$$y = \frac{5-2x}{3}$$
$$x^2 - 2x\left(\frac{5-2x}{3}\right) + \left(\frac{5}{3} - \frac{2x}{3}\right)^2 = 0$$
$$x^2 - \frac{10x}{3} + \frac{4x^2}{3} + \frac{25}{9} - \frac{20x}{9} + \frac{4x^2}{9} = 0$$
$$\frac{25}{9}x^2 - \frac{50}{9}x + \frac{25}{9} = 0$$

Multiply by 9/25

$$x^2 - 2x + 1 = 0$$

This equation can be factored to give two identical factors, leading to two equal roots:

$$(x-1)^2 = 0$$
$$x = 1$$

This gives

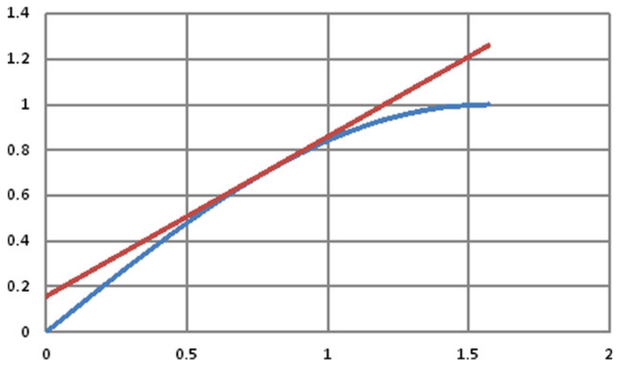
$$2 + 3y = 5$$
$$y = 1$$

Differential Calculus

EXERCISES

Exercise 6.1. Using graph paper plot the curve representing $y = \sin(x)$ for values of x lying between 0 and $\pi/2$ radians. Using a ruler, draw the tangent line at $x = \pi/4$. By drawing a right triangle on your graph and measuring its sides, find the slope of the tangent line.

Your graph should look like this:



The slope of the tangent line should be equal to $\frac{\sqrt{2}}{2} = 0.70717\cdots$

Exercise 6.2. Decide where the following functions are differentiable.

a.

$$y = \frac{1}{1-x}$$

This function has an infinite discontinuity at $x = 1$ and is not differentiable at that point. It is differentiable everywhere else.

b.

$$y = x + 2\sqrt{x}$$

This function has a term, x, that is differentiable everywhere, and a term $2\sqrt{x}$, that is differentiable only for $x \prec 0$.

c.

$$y = \tan(x)$$

This function is differentiable except at $x = \pi/2, 3\pi/2, 5\pi/2, \ldots$

Exercise 6.3. The exponential function can be represented by the following power series

$$e^{bx} = 1 + bx + \frac{1}{2!}b^2x^2 + \frac{1}{3!}b^3x^3 + \cdots + \frac{1}{n!}b^nx^n \cdots$$

where the ellipsis $(\cdots)$ indicates that additional terms follow. The notation $n!$ stands for n *factorial*, which is defined to equal $n(n-1)(n-2)\cdots(3)(2)(1)$ for any positive integral value of n and to equal 1 for $n = 0$. Derive the expression for the derivative of e^{bx} from this series.

$$\begin{aligned}
&\frac{d}{dx}\left(1 + bx + \frac{1}{2!}b^2x^2 + \frac{1}{3!}b^3x^3 + \cdots + \frac{1}{n!}b^nx^n \cdots\right) \\
&= b + 2\left(\frac{1}{2!}b^2x\right) + 3\left(\frac{1}{3!}b^3x2\right) + \cdots + n\left(\frac{1}{n!}b^nx^{n-1}\right)\cdots \\
&= b\left(1 + bx + \frac{1}{2!}b^2x^2 + \frac{1}{3!}b^3x^3 + \cdots + \frac{1}{n!}b^nx^n \cdots\right) \\
&= be^{bx}
\end{aligned}$$

Exercise 6.4. Draw rough graphs of several functions from Table 6.1. Below each graph, on the same sheet of paper, make a rough graph of the derivative of the same function.

Solution not given here.

Exercise 6.5. Assume that $y = 3.00x^2 - 4.00x + 10.00$. If $x = 4.000$ and $\Delta x = 0.500$, Find the value of Δy using Eq. (6.2). Find the correct value of Δy

$$\Delta y \approx \left(\frac{dy}{dx}\right)\Delta x = (6.00x - 4.00)(0.500)$$
$$\times(24.00 - 4.00)(0.500) = 10.00$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00030-6

Now we compute the correct value of Δy:

$$\begin{aligned}
y(4.500) &= (3.00)(4.500^2) - (4.00)(4.500) + 10.00 \\
&= 52.75 \\
y(4.000) &= (3.00)(4.000^2) - (4.00)(4.000) + 10.00 \\
&= 42.00 \\
\Delta y &= y(4.500) - y(4.00) = 52.75 - 42.00 \\
&= 10.75
\end{aligned}$$

Our approximation was wrong by about 7.5%.

Exercise 6.6. Find the following derivatives. All letters stand for constants except for the dependent and independent variables indicated.

a. $\dfrac{dy}{dx}$, where $y = (ax^2 + bx + c)^{-3/2}$

$$\frac{d}{dx}(ax^2+bx+c)^{-3/2} = -\frac{3}{2}\left(\frac{2ax+b}{(ax^2+bx+c)^{-5/2}}\right)$$

b. $\dfrac{d\ln(P)}{dT}$, where $P = ke^{-Q/T}$

$$\begin{aligned}
\ln(P) &= \ln(k) - \frac{Q}{T} \\
\frac{d\ln(P)}{dT} &= -\frac{d(Q/T)}{dT} = \frac{Q}{T^2}
\end{aligned}$$

c. $\dfrac{dy}{dx}$, where $y = a\cos(bx^3)$

$$\begin{aligned}
\frac{d}{dx}a\cos(bx^3) &= -a\sin(bx^3)(3bx^2) \\
&= -3abx^2\sin(bx^3)
\end{aligned}$$

Exercise 6.7. Carry out Newton's method by hand to find the smallest positive root of the equation

$$\begin{aligned}
1.000x^2 - 5.000x + 1.000 &= 0 \\
\frac{df}{dx} &= 2.000x - 5.000
\end{aligned}$$

A graph indicates a root near $x = 0.200$. we take $x_0 = 0.2000$.

$$x_1 = x_0 - \frac{f(x_0)}{f^{(1)}(x_0)}$$

$$\begin{aligned}
f(0.2000) &= 0.04000 - (5.000)(0.200) + 1.000 \\
&= 0.04000 \\
f^{(1)}(0.2000) &= (2.000)(0.2000) - 5.000 = -4.600
\end{aligned}$$

$$x_1 = 0.2000 - \frac{0.04000}{-4.600} = 0.2000 + 0.008696 = 0.208696$$

$$x_2 = x_1 - \frac{f(x_1)}{f^{(1)}(x_1)}$$

$$\begin{aligned}
f(0.208696) &= 0.043554 - (5.000)(0.208696) \\
&\quad + 1.000 = 0.000074 \\
f^{(1)}(0.208696) &= 2(0.208696) - 5.000 = -4.58261
\end{aligned}$$

$$x_2 = 0.208696 + \frac{0.000074}{4.58261} = 0.20871$$

We discontinue iteration at the point, since the second approximation does not differ significantly from the first approximation. This is the correct value of the root to five significant digits.

Exercise 6.8. Find the second and third derivatives of the following functions. Treat all symbols except for the specified independent variable as constants.

a. $y = y(x) = ax^n$

$$\begin{aligned}
\frac{dy}{dx} &= anx^{n-1} \\
\frac{d^2y}{dx^2} &= an(n-1)x^{n-2} \\
\frac{d^3y}{dx^3} &= an(n-1)(n-2)x^{n-3}
\end{aligned}$$

b. $y = y(x) = ae^{bx}$

$$\begin{aligned}
\frac{dy}{dx} &= abe^{bx} \\
\frac{d^2y}{dx^2} &= ab^2e^{bx}a \\
\frac{d^3y}{dx^3} &= ab^3e^{bx}
\end{aligned}$$

Exercise 6.9. Find the curvature of the function $y = \cos(x)$ at $x = 0$ and at $x = \pi/2$.

$$\begin{aligned}
\frac{dy}{dx} &= -\sin(x) \\
\frac{d^2y}{dx^2} &= -\cos(x)
\end{aligned}$$

$$K = \frac{d^2y/dx^2}{\left[1 + \left(\dfrac{dy}{dx}\right)^2\right]^{3/2}} = \frac{-\cos(x)}{\left[1 + (\sin(x))^2\right]^{3/2}}$$

at $x = 0$

$$K = \frac{-1}{1^{3/2}} = -1$$

at $x = \pi/2$.

$$K = \frac{0}{2^{3/2}} = 0$$

Exercise 6.10. For the interval $-10 < x < 10$, find the maximum and minimum values of

$$y = -1.000x^3 + 3.000x^2 - 3.000x + 8.000$$

We take the first derivative:

$$\begin{aligned}\frac{dy}{dx} &= -3.000x^2 + 6.000x - 3.000\\ &= -3.000(x^2 - 2.000x + 1.000)\\ &= -3.000(x - 1.000)^2 = 0 \quad \text{if } x = 1\end{aligned}$$

We test the second derivative to see if we have a relative maximum, a relative minimum, or an inflection point:

$$\begin{aligned}\frac{d^2y}{dx^2} &= -6.000x + 6.000\\ &= 0 \text{ if } x = 1.000\end{aligned}$$

The point $x = 1.000$ is an inflection point. The possible maximum and minimum values are at the ends of the interval

$$\begin{aligned}y_{\max} &= y(-10.000) = 1538\\ y_{\min} &= y(10.000) = -522\end{aligned}$$

The maximum is at $x = -10$ and the minimum is at $x = 10$.

Exercise 6.11. Find the inflection points for the function $y = \sin(x)$. The inflection points occur at points where the second derivative vanishes.

$$\begin{aligned}\frac{dy}{dx} &= \cos(x)\\ \frac{d^2y}{dx^2} &= -\sin(x)\\ \frac{d^2y}{dx^2} &= 0 \text{ when } x = \pm 0, \pm\pi, \pm 2\pi, \pm 3\pi, \ldots\end{aligned}$$

Exercise 6.12. Decide which of the following limits exist and find the values of those that do exist.

a. $\lim_{x\to\pi/2}[x\tan(x)]$ This limit does not exist, since $\tan(x)$ diverges at $x = \pi/2$.
b. $\lim_{x\to 0}[\ln(x)]$. This limit does not exist, since $\ln(x)$ diverges at $x = 0$.

Exercise 6.13. Find the value of the limit:

$$\lim_{x\to 0}\left[\frac{\tan(x)}{x}\right]$$

We apply l'Hôpital's rule.

$$\begin{aligned}\lim_{x\to 0}\left[\frac{\tan(x)}{x}\right] &= \lim_{x\to 0}\left[\frac{d\tan(x)dx}{dx/dx}\right] = \lim_{x\to 0}\left[\frac{\sec^2(x)}{1}\right]\\ &= \lim_{x\to 0}\left[\frac{1}{\cos^2(x)}\right] = 1\end{aligned}$$

Exercise 6.14. Investigate the limit

$$\lim_{x\to\infty}(x^{-n}e^x)$$

for any finite value of n.

$$\lim_{x\to\infty}(x^{-n}e^x) = \lim_{x\to\infty}\left(\frac{e^x}{x^n}\right) = \lim_{x\to\infty}\left(\frac{e^x}{nx^{n-1}}\right)$$

Additional applications of l'Hôpital's rule give decreasing powers of x in the denominator times $n(n-1)(n-2)\cdots$, until we reach a denominator equal to the derivative of a constant, which is equal to zero. The limit does not exist.

Exercise 6.15. Find the limit

$$\lim_{x\to\infty}\left[\frac{\ln(x)}{\sqrt{x}}\right].$$

We apply l'Hôpital's rule.

$$\begin{aligned}\lim_{x\to\infty}\left[\frac{\ln(x)}{\sqrt{x}}\right] &= \lim_{x\to\infty}\left[\frac{1/x}{x^{-1/2}}\right]\\ &= \lim_{x\to\infty}\left[\frac{x^{1/2}}{x}\right] = \lim_{x\to\infty}\left[\frac{1}{\sqrt{x}}\right] = 0\end{aligned}$$

Exercise 6.16. Find the limit

$$\lim_{\nu\to\infty}\left(\frac{Nh\nu}{e^{h\nu/k_BT} - 1}\right)$$

We apply Hôpital's rule

$$\begin{aligned}&\lim_{\nu\to\infty}\left(\frac{Nh\nu}{e^{h\nu/k_BT} - 1}\right)\\ &= \lim_{\nu\to\infty}\left(\frac{Nh}{\frac{h}{k_BT}e^{h\nu/k_BT}}\right)\lim_{\nu\to\infty}\left(\frac{Nk_BT}{e^{h\nu/k_BT}}\right) = 0\end{aligned}$$

Notice that this is the same as the limit taken as $T \to 0$.

PROBLEMS

1. The sine and cosine functions are represented by the two series

$$\begin{aligned}\sin(x) &= x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots\\ \cos(x) &= 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots\end{aligned}$$

Differentiate each series to show that

$$\frac{d\sin(x)}{dx} = \cos(x)$$

and

$$\frac{d\cos(x)}{dx} = -\sin(x)$$

The derivative of the first series is

$$\begin{aligned}\frac{d\sin(x)}{dx} &= 1 - \frac{2x^2}{3!} + \frac{5x^4}{5!} - \frac{yx^6}{7!} + \cdots\\ &= 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots\end{aligned}$$

The derivative of the second series is

$$\begin{aligned}\frac{\mathrm{d}\cos(x)}{\mathrm{d}x} &= -\frac{2x}{2!}+\frac{4x^3}{4!}-\frac{6x^5}{6!}+\cdots\\ &= -\left(1-\frac{x^2}{2!}+\frac{x^4}{4!}-\frac{x^6}{6!}+\cdots\right).\end{aligned}$$

2. The natural logarithm of $1+x$ is represented by the series

$$\ln(1+x) = x-\frac{x^2}{2}+\frac{x^3}{3}-\frac{x^4}{4}\cdots$$
$$(\text{valid for } x^2<1 \text{ and } x=1).$$

Use the identity

$$\frac{\mathrm{d}\ln(x)}{\mathrm{d}x}=\frac{1}{x}.$$

to find a series to represent $1/(1+x)$.

$$\begin{aligned}\frac{\mathrm{d}\ln(1+x)}{\mathrm{d}x} &= \frac{1}{1+x}=\frac{\mathrm{d}}{\mathrm{d}x}\left(x-\frac{x^2}{2}+\frac{x^3}{3}-\frac{x^4}{4}\cdots\right)\\ &= 1-x+x^2-x^3+\cdots\end{aligned}$$

3. Use the definition of the derivative to derive the formula

$$\frac{\mathrm{d}(yz)}{\mathrm{d}x}=y\frac{\mathrm{d}z}{\mathrm{d}x}+z\frac{\mathrm{d}y}{\mathrm{d}x}$$

where y and z are both functions of x.

$$\frac{\mathrm{d}(yz)}{\mathrm{d}x}=\lim_{x_2\to x_1}\frac{y(x_2)z(x_2)-y(x_1)z(x_1)}{x_2-x_1}$$

Work backwards from the desired result:

$$\begin{aligned}y\frac{\mathrm{d}z}{\mathrm{d}x}+z\frac{\mathrm{d}y}{\mathrm{d}x} &= \lim_{x_2\to x_1} y\frac{z(x_2)-z(x_1)}{x_2-x_1}\\ &\quad+\lim_{x_2\to x_1} z\frac{y(x_2)-y(x_1)}{x_2-x_1}\\ &= \lim_{x_2\to x_1}\frac{y(x_2)z(x_2)-y(x_2)z(x_1)}{x_2-x_1}\\ &\quad+\lim_{x_2\to x_1} z\frac{y(x_2)z(x_1)-y(x_1)z(x_1)}{x_2-x_1}\end{aligned}$$

Two terms cancel:

$$y\frac{\mathrm{d}z}{\mathrm{d}x}+z\frac{\mathrm{d}y}{\mathrm{d}x}=\lim_{x_2\to x_1}\frac{y(x_2)z(x_2)-y(x_1)z(x_1)}{x_2-x_1}$$

4. The number of atoms of a radioactive substance at time t is given by

$$N(t)=N_o e^{-t/\tau},$$

where N_o is the initial number of atoms and τ is the relaxation time. For ^{14}C, $\tau = 8320\ y$. Calculate the fraction of an initial sample of ^{14}C that remains after 15.00 years, using Equation (6.10). Calculate the correct fraction and compare it with your first answer.

$$\begin{aligned}\Delta N &\approx \left(\frac{\mathrm{d}N}{\mathrm{d}t}\right)\Delta t = .-\frac{N_o}{\tau}e^{-t/\tau}\Delta t\\ \frac{\Delta N}{N_0} &\approx -\frac{1}{8320\mathrm{y}}e^0(15.00\mathrm{y})'\\ &= 0.001803\\ \text{Fraction remaining} &\approx 1.000000-0.001202\\ &= 0.998197\end{aligned}$$

$$\begin{aligned}\text{Fraction remaining} = .e^{-t/\tau} &= \exp\left(\frac{-15.00}{8320}\right)\\ &= 0.998199\end{aligned}$$

5. Find the first and second derivatives of the following functions

a. $P = P(V_\mathrm{m}) = RT\left(1/V_\mathrm{m}+B/V_\mathrm{m}^2+C/V_\mathrm{m}^3\right)$ where R, B, and C are constants

$$\begin{aligned}\frac{\mathrm{d}P}{\mathrm{d}V_\mathrm{m}} &= RT\left(-1/V_\mathrm{m}^2-2B/V_\mathrm{m}^3-3C/V_\mathrm{m}^4\right)\\ \frac{\mathrm{d}^2P}{\mathrm{d}V_\mathrm{m}^2} &= RT\left(2/V_\mathrm{m}^3+6B/V_\mathrm{m}^4+12C/V_\mathrm{m}^5\right)\end{aligned}$$

b. $G = G(x) = G^\circ + RTx\ln(x) + RT(1-x)\ln(1-x)$, where G°, R, and T are constants

$$\begin{aligned}\frac{\mathrm{d}G}{\mathrm{d}x} &= RT[1+\ln(x)]+RT[-1-\ln(1-x)]\\ \frac{\mathrm{d}^2G}{\mathrm{d}x^2} &= RT\left[\frac{1}{x}\right]+RT\left[\frac{1}{1-x}\right]\end{aligned}$$

c. $y = y(x) = a\ln(x^{1/3})$

$$\frac{\mathrm{d}y}{\mathrm{d}x}=\frac{a}{x^{1/3}}\left(\frac{1}{3}\right)\left(x^{-2/3}\right)=\frac{a}{3x}$$

6. Find the first and second derivatives of the following functions:

a. $y = y(x) = 3x^3\ln(x)$

$$\begin{aligned}\frac{\mathrm{d}y}{\mathrm{d}x} &= 3x^2+9x^2\ln x\\ \frac{\mathrm{d}^2y}{\mathrm{d}x^2} &= 15x+18x\ln x\end{aligned}$$

b. $y = y(x) = 1/(c-x^2)$

$$\begin{aligned}\frac{\mathrm{d}y}{\mathrm{d}x} &= \frac{2x}{(c-x^2)^2}\\ \frac{\mathrm{d}^2y}{\mathrm{d}x^2} &= \frac{2}{(c-x^2)^2}+4x\frac{2x}{(c-x^2)^3}\\ &= \frac{2}{(c-x^2)^2}+\frac{8x^2}{(c-x^2)^3}\end{aligned}$$

c. $y = y(x) = ce^{-a\cos(bx)}$, where a, b, and c are constants

$$\frac{dy}{dx} = ce^{-a\cos(bx)}[ab\sin(bx)]$$
$$\frac{d^2y}{dx^2} = ce^{-a\cos(bx)}[ab^2\cos(bx)] + ce^{-a\cos(bx)}[ab\sin(bx)]^2$$

7. Find the first and second derivatives of the following functions.

a. $y = \left(\frac{1}{x}\right)\left(\frac{1}{1+x}\right)$

$$\frac{dy}{dx} = -\left(\frac{1}{x^2}\right)\left(\frac{1}{1+x}\right) - \left(\frac{1}{x}\right)\left(\frac{1}{(1+x)^2}\right)$$
$$= 2\left(\frac{1}{x^3}\right)\left(\frac{1}{1+x}\right) + \left(\frac{1}{x^2}\right)\left(\frac{1}{(1+x)^2}\right) + \left(\frac{1}{x^2}\right)\left(\frac{1}{(1+x)^2}\right) + 2\left(\frac{1}{x}\right)\left(\frac{1}{(1+x)^3}\right)$$
$$= 2\left(\frac{1}{x^3}\right)\left(\frac{1}{1+x}\right) + 2\left(\frac{1}{x^2}\right)\left(\frac{1}{(1+x)^2}\right) + 2\left(\frac{1}{x}\right)\left(\frac{1}{(1+x)^3}\right)$$

b. $f = f(v) = ce^{-mv^2/(2kT)}$ where m, c, k, and T are constants

$$\frac{df}{dv} = -ce^{-mv^2/(2kT)}\left(\frac{2mv}{2kT}\right)$$
$$= -ce^{-mv^2/(2kT)}\left(\frac{mv}{kT}\right)$$
$$\frac{d^2f}{dv^2} = ce^{-mv^2/(2kT)}\left(\frac{mv}{kT}\right)^2 - ce^{-mv^2/(2kT)}\left(\frac{m}{kT}\right)$$

8. Find the first and second derivatives of the following functions.

a. $y = 3\sin^2(2x) = 3\sin(2x)^2$

$$\frac{dy}{dx} = 12\sin(2x)\cos 2x)$$
$$\frac{d^2y}{dx^2} = 24\cos^2 2x - 24\sin^2 2x$$

b. $y = a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4 + a_5x^5$, where a_0, a_1, and so on, are constants

$$\frac{dy}{dx} = a_1 + 2a_2x + 3a_3x^2 + 4a_4x^3 + 5a_5x^4$$
$$\frac{d^2y}{dx^2} = 2a_2 + 6a_3x + 12a_4x^2 + 20a_5x^3$$

c. $y = a\cos(e^{-bx})$, where a and b are constants

$$\frac{dy}{dx} = ab\sin(e^{-bx})e^{-bx}$$
$$\frac{d^2y}{dx^2} = -ab^2e^{-xb}\sin(e^{-xb}) - ab^2e^{-2xb}(\cos(e^{-xb}))$$

9. Find the second and third derivatives of the following functions. Treat all symbols except for the specified independent variable as constants.

a. $v_{\text{rms}} = v_{\text{rms}}(T) = \sqrt{\frac{3RT}{M}}$

$$\frac{dv_{\text{rms}}}{dT} = \left(\frac{1}{2}\right)\left(\frac{3RT}{M}\right)^{-1/2}$$
$$\frac{d^2v_{\text{rms}}}{dT^2} = -\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)\left(\frac{3RT}{M}\right)^{-3/2}$$
$$= -\left(\frac{1}{4}\right)\left(\frac{3RT}{M}\right)^{-3/2}$$
$$\frac{d^3v_{\text{rms}}}{dT^3} = \left(\frac{1}{4}\right)\left(\frac{3}{2}\right)\left(\frac{3RT}{M}\right)^{-5/2}$$
$$= \left(\frac{3}{8}\right)\left(\frac{3RT}{M}\right)^{-5/2}$$

b. $P = P(V) = \frac{nRT}{(V-nb)} - \frac{an^2}{V^2}$

$$\frac{dP}{dV} = -\frac{nRT}{(V-nb)^2} + 2\frac{an^2}{V^3}$$
$$\frac{d^2P}{dV^2} = 2\frac{nRT}{(V-nb)^3} - 6\frac{an^2}{V^4}$$
$$\frac{d^3P}{dV^3} = -6\frac{nRT}{(V-nb)^4} + 24\frac{an^2}{V^5}$$

10. Find the following derivatives and evaluate them at the points indicated.

a. $(dy/dx)_{x=0}$ if $y = \sin(bx)$, where b is a constant

$$\frac{dy}{dx} = b\cos(bx)$$
$$\left(\frac{dy}{dx}\right)_{x=0} = b\cos(0) = b$$

b. $(df/dt)_{t=0}$ if $f = Ae^{-kt}$, where A and k are constants

$$\frac{df}{dt} = -Ake^{-kt}$$
$$\left(\frac{df}{dt}\right)_{t=0} = -Ake^{0} = -Ak$$

11. Find the following derivatives and evaluate them at the points indicated.

a. $(dy/dx)_{x=1}$, if $y = (ax^3 + bx^2 + cx + 1)^{-1/2}$, where a, b, and c are constants

$$\frac{dy}{dx} = \left(\frac{-1}{2}\right)(ax^3 + bx^2 + cx + 1)^{-3/2} \times (3ax^2 + 2bx + c)$$

$$\left(\frac{dy}{dx}\right)_{x=1} = \left(\frac{-1}{2}\right)(a + b + c + 1)^{-3/2} (3a + 2b + c)$$

b. $(d^2y/dx^2)_{x=0}$, if $y = ae^{-bx}$, where a and b are constants.

$$\frac{dy}{dx} = -abe^{-bx}$$

$$\frac{d^2y}{dx^2} = ab^2e^{-bx}$$

$$\left(\frac{d^2y}{dx^2}\right)_{x=0} = ab^2$$

12. Find the following derivatives

a. $\dfrac{d(yz)}{dx}$, where $y = ax^2$, $z = \sin(bx)$

$$\frac{d(yz)}{dx} = \frac{d}{dx}[ax^2 \sin(bx)] = abx^2 \cos(bx) + 2ax \sin(bx)$$

b. $\dfrac{dP}{dV}$, where $P = \dfrac{nRT}{(V - nb)} - \dfrac{an^2}{V^2}$

$$\frac{dP}{dV} = -\frac{nRT}{(V - nb)^2} + 2\frac{an^2}{V^3}$$

c. $\dfrac{d\eta}{d\lambda}$, where $\eta = \dfrac{2\pi hc^2}{\lambda^5(e^{hc/\lambda kT} - 1)}$

$$\frac{d\eta}{d\lambda} = \frac{d}{d\lambda}[2\pi hc^2\lambda^{-5}(e^{hc/\lambda kT} - 1)^{-1}]$$
$$= -10\pi hc^2\lambda^{-6}(e^{hc/\lambda kT} - 1)^{-1} - 2\pi hc^2\lambda^{-5}(e^{hc/\lambda kT} - 1)^{-2} \times e^{hc/\lambda kT}\left(-\frac{hc}{\lambda^2 kT}\right)$$
$$= -\frac{10\pi hc^2}{\lambda^6(e^{hc/\lambda kT} - 1)} - \frac{2\pi h^2c^3e^{hc/\lambda kT}}{\lambda^7 kT(e^{hc/\lambda kT} - 1)^2}$$

13. Find a formula for the curvature of the function

$$P(V) = \frac{nRT}{V - nb} - \frac{an^2}{V^2}.$$

where n, R, a, b, and T are constants

$$K = \frac{d^2y/dx^2}{[1 + (dy/dx)^2]^{3/2}}$$

$$\frac{dP}{dV} = -\frac{nRT}{(V - nb)^2} + 2\frac{an^2}{V^3}$$

$$\frac{d^2P}{dV^2} = 2\frac{nRT}{(V - nb)^3} - 6\frac{an^2}{V^4}$$

$$K = \frac{2\dfrac{nRT}{(V - nb)^3} - 6\dfrac{an^2}{V^4}}{\left[1 + \left(-\dfrac{nRT}{(V - nb)^2} + 2\dfrac{an^2}{V^3}\right)^2\right]^{3/2}}$$

14. The volume of a cube is given by

$$V = V(a) = a^3,$$

where a is the length of a side. Estimate the percent error in the volume if a 1.00% error is made in measuring the length, using the formula

$$\Delta V \approx \left(\frac{dV}{da}\right)\Delta a.$$

Check the accuracy of this estimate by comparing $V(a)$ and $V(1.01a)$.

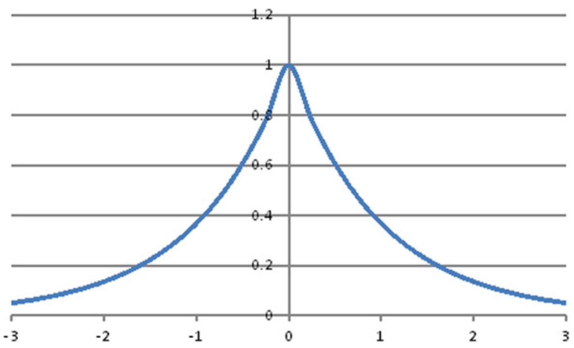
$$\frac{\Delta V}{V} \approx \frac{1}{V}\left(\frac{dV}{da}\right)\Delta a = \frac{1}{V}(3a^2)\Delta a = \frac{1}{a^3}(3a^2)\Delta a = \frac{3\Delta a}{a} = 0.0300$$

$$\frac{V(1.0100) - V(1.000)}{V(1.000)} = \frac{(1.0100)^3 - 1.0000}{1.00000} = 0.030301$$

15. Draw a rough graph of the function

$$y = y(x) = e^{-|x|}$$

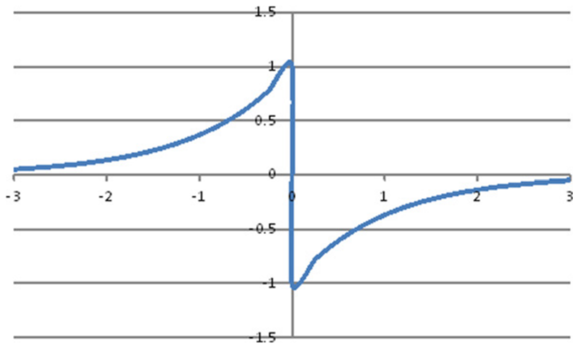
Your graph of the function should look like this:



Is the function differentiable at $x = 0$? Draw a rough graph of the derivative of the function.

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \begin{cases} -e^{-x} & \text{if} \quad x \succeq 0 \\ e^{x} & \text{if} \quad x \preccurlyeq 0 \end{cases}$$

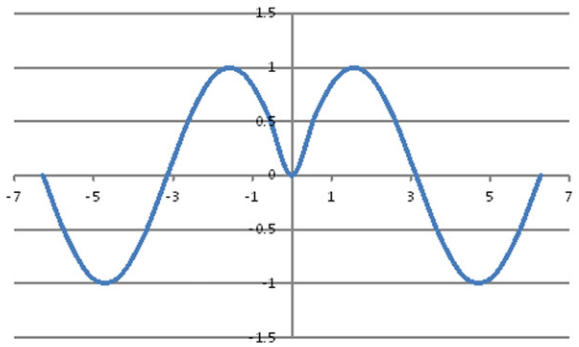
The function is not differentiable at $x = 0$. Your graph of the derivative should look like this:



16. Draw a rough graph of the function

$$y = y(x) = \sin(|x|)$$
$$y = \begin{cases} \sin(-x) & \text{if} \quad x \prec 0 \\ \sin(x) & \text{if} \quad x \prec 0 \end{cases}$$

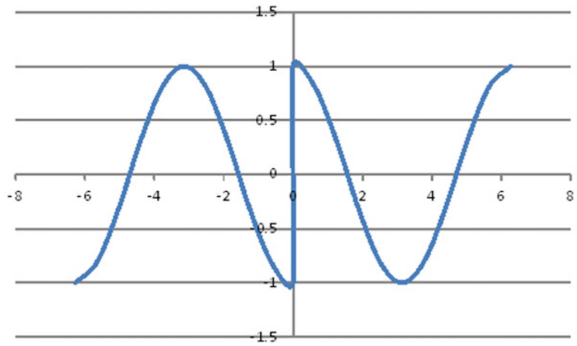
Your graph should look like this:



Is the function differentiable at $x = 0$? The function is not differentiable at $x = 0$. Draw a rough graph of the derivative of the function. The derivative of the function is

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \begin{cases} -\cos(-x) = -\cos(x) & \text{if } x \prec 0 \\ \cos(x) & \text{if } x \prec 0 \end{cases}$$

Your graph of the derivative should look like this:



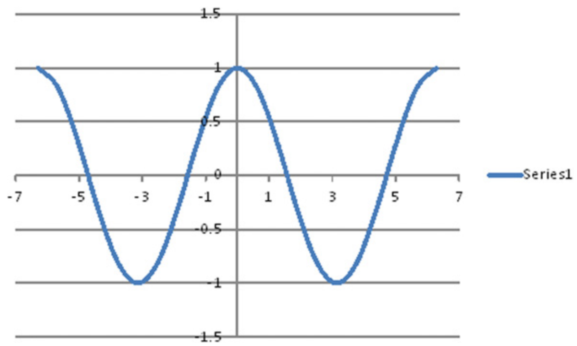
17. Draw a rough graph of the function

$$y = y(x) = \cos(|x|)$$

Is the function differentiable at $x = 0$? Since the cosine function is an even function

$$\cos(|x|) = \cos(x)$$

The function is differentiable at all points. Draw a rough graph of the derivative of the function, your graph of the function should look like a graph of the cosine function:



18. Show that the function $\psi = \psi(x) = A\sin(kx)$ satisfies the equation

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi$$

if A and k are constants.

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = Ak\cos(kx)$$
$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -Ak^2\sin(kx) = -k^2\psi$$

19. Show that the function $\psi(x) = \cos(kx)$ satisfies the equation

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi$$

if A and k are constants.

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = -k\sin(kx)$$
$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\cos(kx) = -k^2\psi$$

20. Draw rough graphs of the third and fourth derivatives of the function whose graph is given in Fig. 6.6.

21. The mean molar Gibbs energy of a mixture of two enantiomorphs (optical isomers of the same substance) is given at a constant temperature T by

$$\begin{aligned} G_m &= G_m(x) \\ &= G_m^\circ + RTx\ln(x) + RT(1-x)\ln(1-x) \end{aligned}$$

where x is the mole fraction of one of them. G_m° is a constant, R is the ideal gas constant, and T is the constant temperature. What is the concentration of each enantiomorph when G has its minimum value? What is the maximum value of G in the interval $0 \leqslant x \leqslant 1$?

$$\frac{\mathrm{d}G_m}{\mathrm{d}x} = RT[1+\ln(x)] + RT[-1-\ln(1-x)]$$

This derivative vanishes when

$$\begin{aligned} 1+\ln(x)-1-\ln(1-x) &= 0 \\ \ln(x)-\ln(1-x) &= 0 \\ \ln\left(\frac{x}{1-x}\right) &= 0 \\ \frac{x}{1-x} &= 1 \\ x &= 1-x \\ x &= \frac{1}{2} \end{aligned}$$

The minimum occurs at $x = 1/2$. There is no relative maximum. To find the maximum, consider the endpoints of the interval:

$$G_m(0) = G_m^\circ + RT\lim_{x\to 0}[x\ln(x)]$$

Apply l'Hôpital's rule

$$\lim_{x\to 0}\frac{\ln(x)}{x^{-1}} = \lim_{x\to 0}\frac{1/x}{-1/x^2} = \lim_{x\to 0}(x) = 0$$

The same value occurs at $x = 1$, since $1-x$ plays the same role in the function as does x. The maximum value of the function is

$$G_m(0) = G_m(1) = G_m^\circ$$

22. A rancher wants to enclose a rectangular part of a large pasture so that $1.000\ \mathrm{km}^2$ is enclosed with the minimum amount of fence.

a. Find the dimensions of the rectangle that he should choose. The area is

$$A = xy$$

but A is fixed at $1.000\ \mathrm{km}^2$, so that $y = A/x$. The perimeter of the area is

$$p = 2x + 2y = 2x + \frac{2A}{x}$$

To minimize the perimeter, we find

$$\begin{aligned} \frac{\mathrm{d}p}{\mathrm{d}x} &= 2 - \frac{2A}{x^2} = 0 \\ x^2 &= A \\ x &= \sqrt{A} = 1.000\ \mathrm{km} = 1000\ \mathrm{m} \end{aligned}$$

The area is a square.

b. The rancher now decides that the fenced area must lie along a road and finds that the fence costs \$20.00 per meter along the road and \$10.00 per meter along the other edges. Find the dimensions of the rectangle that would minimize the cost of the fence. The cost of the fence is

$$c = (\$20.00)x + \frac{(\$10.00)A}{x}$$

$$\begin{aligned} \frac{\mathrm{d}c}{\mathrm{d}x} &= \$20.00 - \frac{(\$10.00)A}{x^2} \\ x^2 &= \frac{(\$10.00)A}{(\$20.00)^2} = 0.025A \\ x &= 0.1581\sqrt{A} = 0.1581(1000\ \mathrm{m}) = 158\ \mathrm{m} \end{aligned}$$

The area has 158 m along the road, and 6325 m in the other direction.

23. The sum of two nonnegative numbers is 100. Find their values if their product plus twice the square of the first is to be a maximum. We denote the first number by x and let

$$\begin{aligned} f &= x(100-x) + 2x^2 \\ \frac{\mathrm{d}f}{\mathrm{d}x} &= 100 - 2x + 4x = 100 + 2x \end{aligned}$$

At an extremum

$$0 = 100 + 2x$$

This corresponds to $x = -50$. Since we specified that the numbers are nonzero, we inspect the ends of the region.

$$\begin{aligned} f(0) &= 0 \\ f(100) &= 20000 \end{aligned}$$

The maximum corresponds to $x = 100$.

24. A cylindrical tank in a chemical factory is to contain 2.000 m^3 of a corrosive liquid. Because of the cost of the material, it is desirable to minimize the area of the tank. Find the optimum radius and height and find the resulting area. We let the radius be r and the height be h.

$$V = \pi r^2 h = 2.000\ \mathrm{m}^3$$
$$h = \frac{2.000\ \mathrm{m}^3}{\pi r^2}$$

$$\begin{aligned} A &= 2\pi r^2 + 2\pi r h \\ &= 2\pi r^2 + 2\pi r\left(\frac{V}{\pi r^2}\right) = 2\pi r^2 + \frac{2V}{r} \end{aligned}$$

To minimize A we let

$$\frac{\mathrm{d}A}{\mathrm{d}r} = 4\pi r - \frac{2V}{r^2} = 0$$

$$\begin{aligned} r^3 &= \frac{2V}{4\pi} = \frac{V}{2\pi} = \frac{1.000\ \mathrm{m}^3}{\pi} = 0.3183\ \mathrm{m}^3 \\ r &= (0.3183\ \mathrm{m}^3)^{1/3} = 0.6828\ \mathrm{m} \\ h &= \frac{2.000\ \mathrm{m}^3}{\pi(0.6828\ \mathrm{m})^2} = 1.366\ \mathrm{m} \\ A &= 2\pi(0.6828\ \mathrm{m})^2 + 2\pi(0.6828\ \mathrm{m})(1.366\ \mathrm{m}) \\ &= 2.929\ \mathrm{m}^3 + 5.860\ \mathrm{m}^3 = 8.790\ \mathrm{m}^3 \\ V &= \pi r^2 h = \pi(0.6828\ \mathrm{m})^2(1.366\ \mathrm{m}) = 2.000\ \mathrm{m}^3 \end{aligned}$$

25. Find the following limits.

a. $\lim_{x\to\infty}[\ln(x)/x^2]$ Apply l'Hôpital's rule:

$$\lim_{x\to\infty}[\ln(x)/x^2] = \lim_{x\to\infty}\left[\frac{1/x}{2x}\right] = 0$$

b. $\lim_{x\to 3}[(x^3-27)/(x^2-9)]$ Apply l'Hôpital's rule:

$$\begin{aligned} \lim_{x\to 3}\left[\frac{(x^3-27)}{(x^2-9)}\right] &= \lim_{x\to 3}\left[\frac{3x^2}{2x}\right] \\ &= \lim_{x\to 3}\left[\frac{3x}{2}\right] = \frac{9}{2} \end{aligned}$$

c. $\lim_{x\to\infty}\left[x\ln\left(\frac{1}{1+x}\right)\right]$

$$\begin{aligned} \lim_{x\to\infty}\left[x\ln\left(\frac{1}{1+x}\right)\right] &= \lim_{x\to\infty}\left[\frac{\ln\left(\frac{1}{1+x}\right)}{1/x}\right] \\ &= \lim_{x\to\infty}\left[\frac{-\ln(1+x)}{1/x}\right] \end{aligned}$$

Apply l'Hôpital's rule:

$$\begin{aligned} \lim_{x\to\infty}\left[\frac{-\ln(1+x)}{1/x}\right] &= \lim_{x\to\infty}\left[\frac{-1/(1+x)}{-1/x^2}\right] \\ &= \lim_{x\to\infty}\left[\frac{x^2}{1+x}\right] \end{aligned}$$

This diverges and the limit does not exist.

26. Find the following limits.

a. $\lim_{x\to 0^+}\left[\frac{\ln(1+x)}{\sin(x)}\right]$ Apply l'Hôpital's rule:

$$\lim_{x\to 0^+}\left[\frac{\ln(1+x)}{\sin(x)}\right] = \lim_{x\to 0^+}\left[\frac{1/(1+x)}{\cos(x)}\right] = 1$$

b. $\lim_{x\to 0^+}[\sin(x)\ln(x)]$

$$\lim_{x\to 0^+}[\sin(x)\ln(x)] = \lim_{x\to 0^+}\left[\frac{\ln(x)}{1/\sin(x)}\right]$$

Apply l'Hôpital's rule:

$$\begin{aligned} &\lim_{x\to 0^+}\left[\frac{\ln(x)}{1/\sin(x)}\right] \\ &= \lim_{x\to 0^+}\left[\frac{1/x}{-[1/\sin^2(x)]\cos(x)}\right] \\ &= \lim_{x\to 0^+}\left[\frac{-\sin^2(x)}{x\cos(x)}\right] \end{aligned}$$

Apply l'Hôpital's rule again

$$\begin{aligned} &\lim_{x\to 0^+}\left[\frac{-\sin^2(x)}{x\cos(x)}\right] \\ &= \lim_{x\to 0^+}\left[\frac{-2\sin(x)\cos(x)}{\cos(x)-x\sin(x)}\right] = 0 \end{aligned}$$

27. Find the following limits

a. $\lim_{x\to\infty}(e^{-x^2}/e^{-x})$.

$$\lim_{x\to\infty}\left(\frac{e^{-x^2}}{e^{-x}}\right) = \lim_{x\to\infty}(e^{-x^2+x}) = 0$$

b. $\lim_{x\to 0}[x^2/(1-\cos(2x))]$. Apply l'Hôpital's rule twice:

$$\begin{aligned} &\lim_{x\to 0}\left[\frac{x^2}{1-\cos(2x)}\right] \\ &= \lim_{x\to 0}\left[\frac{2x}{2\sin(2x)}\right] = \lim_{x\to 0}\left[\frac{2}{4\cos(2x)}\right] = \frac{1}{2} \end{aligned}$$

c. $\lim_{x\to\pi}[\sin(x)/\sin(3x/2)]$. Apply l'Hôpital's rule

$$\lim_{x\to\pi}\left[\frac{\sin(x)}{\sin(3x/2)}\right]\lim_{x\to\pi}\left[\frac{\cos(x)}{3\cos 3x)/2}\right] = \frac{2}{3}$$

28. Find the maximum and minimum values of the function

$$y = x^3 - 4x^2 - 10x$$

in the interval $-5 < x < 5$.

$$\frac{dy}{dx} = 3x^2 - 8x - 10$$

A relative extremum corresponds to

$$\begin{aligned} 3x^2 - 8x - 10 &= 0 \\ x &= \frac{8 \pm \sqrt{64+120}}{6} = \frac{8 \pm 13.56}{6} \\ &= \frac{4}{3} \pm 2.26 = \begin{cases} 3.594 \\ -0.927 \end{cases} \end{aligned}$$

$$\begin{aligned} y(3.594) &= -41.18 \\ y(-0.927) &= 5.036 \\ y(-5) &= -175 \\ y(5) &= -25 \end{aligned}$$

The minimum is at $x = -5$, and the maximum is at $x = -0.927$.

29. If a hydrogen atom is in a $2s$ state, the probability of finding the electron at a distance r from the nucleus is proportional to $4\pi r^2 \psi_{2s}^2$ where ψ represents the orbital (wave function):

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0},$$

where a_0 is a constant known as the Bohr radius, equal to 0.529×10^{-10} m.

a. Locate the maxima and minima of ψ_{2s}. To find the extrema, we omit the constant factor:

$$\begin{aligned} &\frac{d}{dr}\left[\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}\right] \\ &\quad = \left(\frac{-1}{a_0}\right) e^{-r/2a_0} + \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \left(\frac{-1}{2a_0}\right) = 0 \end{aligned}$$

We cancel the exponential factor, which is the same in all terms:

$$\begin{aligned} \left(\frac{-1}{a_0}\right) + \left(2 - \frac{r}{a_0}\right)\left(\frac{-1}{2a_0}\right) &= 0 \\ -\frac{2}{a_0} + \frac{r}{2a_0^2} &= 0 \end{aligned}$$

At the relative extremum

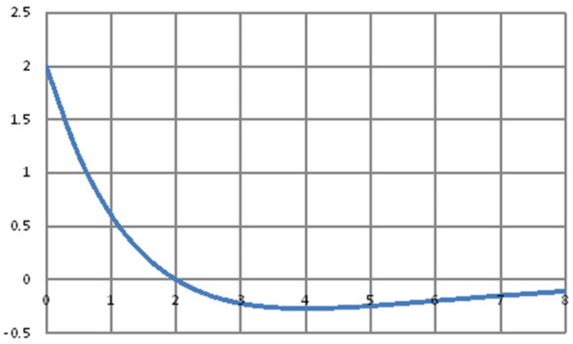
$$r = 4a_0$$

This is a relative minimum, since the function is negative at this point. The function approaches zero as r becomes large, so the maximum is at $r = 0$.

b. Draw a rough graph of ψ_{2s}. For a rough graph, we omit the constant factor and let $r/a_0 = u$. We graph the function

$$f = (2 - u)e^{-u/2}$$

your graph should look like this:



c. Locate the maxima and minima of ψ_{2s}^2.

$$\psi_{2s}^2 = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{32\pi}\right) \left(\frac{1}{a_0}\right)^3 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0},$$

To locate the extrema, we omit the constant factor

$$\begin{aligned} &\frac{d}{dr}\left[\left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}\right] \\ &\quad = \frac{d}{dr}\left[\left(4 - \frac{4r}{a_0} + \frac{r^2}{a_0^2}\right) e^{-r/a_0}\right] \\ &\quad = \left(-\frac{4}{a_0} + \frac{2r}{a_0^2}\right) e^{-r/a_0} \\ &\qquad + \left(4 - \frac{4r}{a_0} + \frac{r^2}{a_0^2}\right) e^{-r/a_0} \left(\frac{-1}{a_0}\right) = 0 \end{aligned}$$

Cancel the exponential term:

$$\begin{aligned} -\frac{4}{a_0} + \frac{2r}{a_0^2} - \left(\frac{4}{a_0} - \frac{4r}{a_0^2} + \frac{r^2}{a_0^3}\right) &= 0 \\ -\frac{4}{a_0} + \frac{2r}{a_0^2} - \frac{4}{a_0} + \frac{4r}{a_0^2} - \frac{r^2}{a_0^3} &= 0 \\ -\frac{8}{a_0} + \frac{6r}{a_0^2} - \frac{r^2}{a_0^3} &= 0 \end{aligned}$$

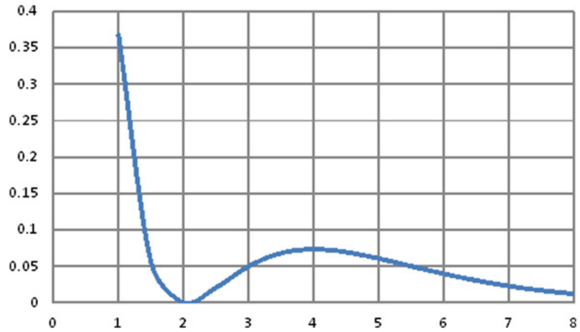
Let $u = r/a_{0:}$ and multiply by a_0

$$u^2 - 6u + 8 = (x-2)(x-4) = 0$$

The relative extrema occur at $x = 3$ and $x = 4$. The first is a relative minimum, where $f = 0$, and the second is a relative maximum.

d. Draw a rough graph of ψ_{2s}^2. For a rough graph, we plot

$$f(u) = (2-u)^2 e^{-u}$$



e. Locate the maxima and minima of $4\pi r^2 \psi_{2s}^2$.

$$4\pi r^2 \psi_{2s}^2 = \frac{4\pi}{4\sqrt{2\pi}} \left(\frac{1}{32\pi}\right)\left(\frac{1}{a_0}\right)^3 r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}$$
$$= \frac{1}{32\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^3 \left(2r - \frac{r^2}{a_0}\right)^2 e^{-r/a_0}$$

To locate the relative extrema, we omit the constant factor

$$\frac{df}{dr} = \frac{d}{dr}\left(2r - \frac{r^2}{a_0}\right)^2 e^{-r/a_0}$$
$$= 2\left(2r - \frac{r^2}{a_0}\right)\left(2 - \frac{2r}{a_0}\right) e^{-r/a_0}$$
$$+ \left(2r - \frac{r^2}{a_0}\right)^2 e^{-r/a_0} \left(\frac{-1}{a_0}\right) = 0$$

We cancel the exponential factor

$$\left(4r - \frac{2r^2}{a_0}\right)\left(2 - \frac{2r}{a_0}\right) - \left(2r - \frac{r^2}{a_0}\right)^2 \left(\frac{1}{a_0}\right) = 0$$
$$\left(8r - \frac{12r^2}{a_0} + \frac{4r^3}{a_0^2}\right) - \left(\frac{4r^2}{a_0} - \frac{4r^3}{a_0^2} + \frac{r^4}{a_0^3}\right) = 0$$

Divide by a_0, replace r/a_0 by u and collect terms:

$$8u - 16u^2 + 8u^3 - u^4 = 0$$

We multiply by -1

$$u(-8 + 16u - 8u^2 + u^3) = 0$$

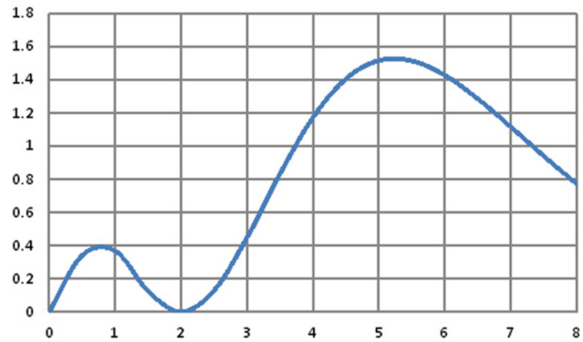
One root is $u = 0$. The roots from the cubic factor are

$$u = \begin{cases} 0.763\,93 \\ 2 \\ 5.236\,1 \end{cases}$$

The two minima are at $r = 0$ and at $r = 2a_0$, and the maximum is at $r = 5.236\,1 a_0$

f. Draw a rough graph of $4\pi r^2 \psi_{2s}^2$. For our rough graph, we plot

$$f = (2u - u^2)^2 e^{-u}$$



30. The probability that a molecule in a gas will have a speed v is proportional to the function

$$f_v(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)$$

where m is the mass of the molecule, k_B is Boltzmann's constant, and T is the temperature on the Kelvin scale. The most probable speed is the speed for which this function is at a maximum. Find the expression for the most probable speed and find its value for nitrogen molecules at $T = 298$ K. Remember to use the mass of a molecule, not the mass of a mole. To find the maximum, we ignore the constant factor:

$$\frac{dg}{dv} = 2v \exp\left(\frac{-mv^2}{2k_B T}\right)$$
$$+ v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)\left(\frac{-2mv}{2k_B T}\right) = 0$$

we cancel the exponential factor and denote the most probable speed by v_p

$$2v_p + v_p^2 \left(\frac{-mv_p}{k_B T}\right) = 0$$
$$v_p \left[2 - \left(\frac{mv_p^2}{k_B T}\right)\right] = 0$$
$$v_p = \sqrt{\frac{2k_B T}{m}}$$

$$m = \frac{M}{N_{Av}} = \frac{0.028014 \text{ kg mol}^{-1}}{6.0221367 \times 10^{23} \text{ mol}^{-1}}$$
$$= 4.652 \times 10^{-26} \text{ kg}$$

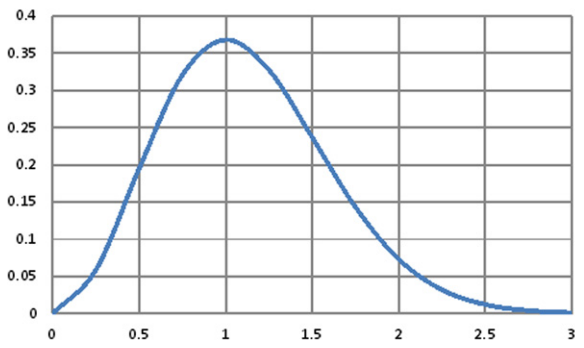
where M is the molar mass and N_{Av} is Avogadro's constant:

$$\begin{aligned} v_p &= \sqrt{2mk_{\mathrm{B}}T} \\ &= \left[\frac{2(1.3806568\times10^{-23}\ \mathrm{J\ K^{-1}})(298.15\ \mathrm{K})}{(4.652\times10^{-26}\ \mathrm{kg})}\right]^{1/2} \\ &= 420.7\ \mathrm{m\ s^{-1}} \end{aligned}$$

For a rough graph, we omit a constant factor and plot the function

$$g = u^2 e^{-u^2}$$

where $u = v/v_p$.



31. According to the Planck theory of black-body radiation, the radiant spectral emittance is given by the formula

$$\eta = \eta(\lambda) = \frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda k_{\mathrm{B}}T}-1)},$$

where λ is the wavelength of the radiation, h is Planck's constant, k_{B} is Boltzmann's constant, c is the speed of light, and T is the temperature on the Kelvin scale. Treat T as a constant and find an equation that gives the wavelength of maximum emittance.

$$\begin{aligned} \frac{d\eta}{d\lambda} &= (2\pi hc^2)\left[\frac{-5}{\lambda^6(e^{hc/\lambda k_{\mathrm{B}}T}-1)}\right. \\ &\quad \left. -\frac{1}{\lambda^5(e^{hc/\lambda k_{\mathrm{B}}T}-1)^2}e^{hc/\lambda k_{\mathrm{B}}T}\left(\frac{-hc}{\lambda^2 k_{\mathrm{B}}T}\right)\right] \end{aligned}$$

At the maximum, this derivative vanishes. We place both terms in the square brackets over a common denominator and set this factor equal to zero.

$$\frac{-5(e^{hc/\lambda k_{\mathrm{B}}T}-1)+e^{hc/\lambda kT}(hc/\lambda k_{\mathrm{B}}T)}{\lambda^6(e^{hc/\lambda k_{\mathrm{B}}T}-1)^2} = 0$$

We set the numerator equal to zero

$$-5(e^{hc/\lambda kT}-1)+e^{hc/\lambda k_{\mathrm{B}}T}(hc/\lambda k_{\mathrm{B}}T) = 0$$

We let $x = hc/\lambda k_{\mathrm{B}}T$ so that

$$-5(e^x-1)+e^x x = 0$$

We divide by e^x

$$-5(1-e^{-x})+x = 0$$

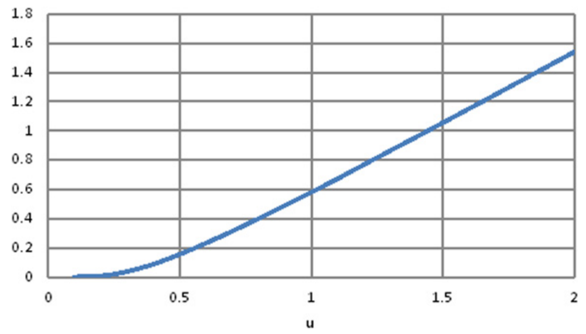
This equation is solved numerically to give $x = 4.965$

$$\lambda_{\max} = \frac{hc}{k_{\mathrm{B}}Tx} = \frac{hc}{4.965k_{\mathrm{B}}T}$$

32. The thermodynamic energy of a collection of N harmonic oscillators (approximate representations of molecular vibrations) is given by

$$U = \frac{Nh\nu}{e^{h\nu/k_{\mathrm{B}}T}-1}$$

a. Draw a rough sketch of the thermodynamic energy as a function of T. Here is an accurate graph. For this graph, we omit the constant $Nh\nu$ and plot the variable $u = k_{\mathrm{B}}T/h\nu$.



b. The heat capacity of this system is given by

$$C = \frac{dU}{dT}.$$

Show that the heat capacity is given by

$$C = Nk_{\mathrm{B}}\left(\frac{h\nu}{k_{\mathrm{B}}T}\right)^2\frac{e^{h\nu/k_{\mathrm{B}}T}}{(e^{h\nu/k_{\mathrm{B}}T}-1)^2}.$$

$$\begin{aligned} C &= \frac{dU}{dT} = \frac{d}{dT}\left[\frac{Nh\nu}{e^{h\nu/k_{\mathrm{B}}T}-1}\right] \\ &= \frac{-Nh\nu}{(e^{h\nu/k_{\mathrm{B}}T}-1)^2}e^{h\nu/k_{\mathrm{B}}T}\left(\frac{-h\nu}{k_{\mathrm{B}}T^2}\right) \\ &= Nk_{\mathrm{B}}\left(\frac{h\nu}{k_{\mathrm{B}}T}\right)^2\frac{e^{h\nu/k_{\mathrm{B}}T}}{(e^{h\nu/k_{\mathrm{B}}T}-1)^2} \end{aligned}$$

c. Find the limit of the heat capacity as $T \to 0$ and as $T \to \infty$. Note that the limit as $T \to \infty$ is the same as the limit $\nu \to 0$.

$$\lim_{T\to0} C = \lim_{T\to0}\left[Nk_{\mathrm{B}}\left(\frac{h\nu}{k_{\mathrm{B}}T}\right)^2\frac{e^{h\nu/k_{\mathrm{B}}T}}{(e^{h\nu/k_{\mathrm{B}}T}-1)^2}\right]$$

In this limit, the 1 in the denominator becomes negligible.

$$\begin{aligned}
\lim_{T\to 0} C &= \lim_{T\to 0}\left[Nk_B\left(\frac{h\nu}{k_BT}\right)^2\frac{e^{h\nu/k_BT}}{(e^{h\nu/k_BT}-1)^2}\right]\\
&= \lim_{T\to 0}\left[Nk_B\left(\frac{h\nu}{k_BT}\right)^2\frac{e^{h\nu/k_BT}}{(e^{h\nu/k_BT})^2}\right]\\
&= \lim_{T\to 0}\left[Nk_B\left(\frac{h\nu}{k_BT}\right)^2\frac{1}{e^{h\nu/k_BT}}\right]\\
&= \lim_{T\to 0}\left[Nk_B\left(\frac{h\nu}{k_BT}\right)^2 e^{-h\nu/k_BT}\right]\\
&= \left(\frac{Nh^2\nu^2}{k_B}\right)\lim_{T\to 0}\left[\frac{e^{-h\nu/k_BT}}{T^2}\right] = 0\\
\lim_{T\to\infty} C &= \lim_{\nu\to 0} C\\
&= \lim_{\nu\to 0}\left[Nk_B\left(\frac{h\nu}{k_BT}\right)^2\frac{e^{h\nu/k_BT}}{(e^{h\nu/k_BT}-1)^2}\right]\\
&= Nk_B\left(\frac{h}{k_BT}\right)^2\lim_{\nu\to 0}\left[\frac{\nu^2 e^{h\nu/k_BT}}{(e^{h\nu/k_BT}-1)^2}\right]\\
&= Nk_B\left(\frac{h}{k_BT}\right)^2\lim_{\nu\to 0}\left[\frac{\nu^2}{(e^{h\nu/k_BT}-1)^2}\right]
\end{aligned}$$

As $\nu \to 0$

$$e^{h\nu/k_BT} - 1 \to 1 + \frac{h\nu}{k_BT} - 1 \to \frac{h\nu}{k_BT}$$

$$Nk_B\left(\frac{h}{k_BT}\right)^2\lim_{\nu\to 0}\left[\frac{\nu^2}{(e^{h\nu/k_BT}-1)^2}\right]$$

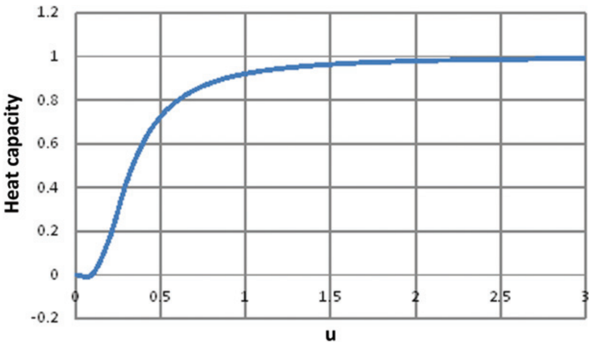
$$= Nk_B\left(\frac{h}{k_BT}\right)^2\lim_{\nu\to 0}\left[\frac{\nu^2}{(h\nu/k_BT)^2}\right]$$

Apply l'Hôpital's rule

$$\begin{aligned}
&\lim_{\nu\to 0}\left[\frac{\nu^2}{(e^{h\nu/k_BT}-1)^2}\right]\\
&= \lim_{\nu\to 0}\left[\frac{2\nu}{(e^{h\nu/k_BT}-1)e^{h\nu/k_BT}(-h\nu/k_BT)}\right]\\
&= Nk_B\left(\frac{h}{k_BT}\right)^2\lim_{\nu\to 0}\left[\frac{1}{(h/k_BT)^2}\right] = Nk_B
\end{aligned}$$

d. Draw a rough graph of C as a function of T. For the rough graph, we use the variable $u = k_BT/h\nu$ and plot C/Nk_B.

$$C \propto Nk_B\left(\frac{1}{u^2}\right)\frac{e^{1/u}}{(e^{1/u}-1)^2}$$



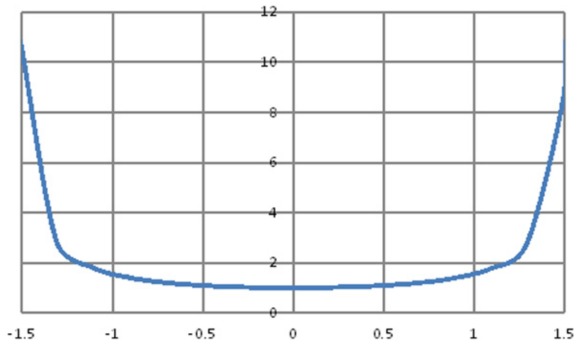
The limit of C as $T \to \infty$ is Nk_B

33. Draw a rough graph of the function

$$y = \frac{\tan(x)}{x}$$

in the interval $-\pi < x < \pi$. Use l'Hôpital's rule to evaluate the function at $x = 0$. Here is an accurate graph. The function diverges at $x = -\pi/2$ and $x = \pi/2$ so we plot only from 1.5 to 1.5. At $x = 0$

$$\lim_{x\to 0}\frac{\tan(x)}{x} = \lim_{x\to 0}\frac{\sec^2(x)}{1} = \frac{\sec^2(0)}{1} = 1$$



34. Find the relative maxima and minima of the function $f(x) = x^3 + 3.00x^2 - 2.00x$ for all real values of x.

$$\begin{aligned}
\frac{df}{dx} &= 3.00x^2 + 6.00x - 2.00 = 0\\
x &= \frac{-6.00 \pm \sqrt{36.00 + 24.00}}{6.00}\\
&= \frac{-6.00 \pm \sqrt{60.00}}{6.00} = \begin{cases} 0.291 \\ -2.291 \end{cases}
\end{aligned}$$

The second derivative is

$$\frac{d^2f}{dx^2} = 6.00x + 6.00$$

At $x = 0.291$ the second derivative is positive, so this represents a relative minimum. At $x = -2.291$ the second derivative is negative, so this represents a relative maximum.

35. The van der Waals equation of state is

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

When the temperature of a given gas is equal to its critical temperature, the gas has a state at which the pressure as a function of V at constant T and n exhibits an inflection point at which $\mathrm{d}P/\mathrm{d}V=0$ and $\mathrm{d}^2P/\mathrm{d}V^2=0$. This inflection point corresponds to the critical point of the gas. Write P as a function of T, V, and $n$and write expressions for $\mathrm{d}P/\mathrm{d}V$ and $\mathrm{d}^2P/\mathrm{d}V^2$, treating T and n as constants. Set these two expressions equal to zero and solve the simultaneous equations to find an expression for the pressure at the critical point.

$$\begin{aligned}
P &= \frac{nRT}{V-nb}-\frac{n^2a}{V^2}\\
\frac{\mathrm{d}P}{\mathrm{d}V} &= -\frac{nRT}{(V-nb)^2}+\frac{2n^2a}{V^3}\\
&= 0 \text{ at the critical point} \qquad (6.1)\\
\frac{\mathrm{d}^2P}{\mathrm{d}V^2} &= \frac{2nRT}{(V-nb)^3}+\frac{6n^2a}{V^4}\\
&= 0 \text{ at the critical point} \qquad (6.2)
\end{aligned}$$

Solve Eq. (6.1) for T_c:

$$T_c=\frac{2n^2a(V_c-nb)^2}{nRV_c^3} \qquad (6.3)$$

Substitute this expression into Eq. (6.2):

$$\begin{aligned}
0 &= -\left(\frac{2nR}{(V-nb)^3}\right)\left(\frac{2n^2a(V-nb)^2}{nRV^3}\right)+\frac{6n^2a}{V^4}\\
0 &= -\frac{4n^2a}{(V-nb)}+\frac{6n^2a}{V}\\
0 &= -\frac{2}{(V-nb)}+\frac{3}{V} \text{ when } V=V_c\\
V_c &= 3nb
\end{aligned}$$

Substitute this into Eq. (6.3)

$$T_c=\frac{2n^2a(2nb)^2}{nR(27n^3b^3)}=\frac{8a}{27Rb}$$

$$\begin{aligned}
P_c &= \frac{nRT_c}{V_c-nb}-\frac{n^2a}{V_c^2}=\frac{8nRa}{27Rb(2nb)}-\frac{n^2a}{9n^2b^2}\\
&= \frac{4a}{27b^2}-\frac{a}{9b^2}=\frac{a}{27b^2}
\end{aligned}$$

36. Carry out Newton's method to find the smallest positive root of the equation

$$5.000x-e^x=0$$

Do the calculation by hand, and verify your result by use of Excel. A graph indicates a root near $x=0.300$. we take $x_0=0.300$.

$$\begin{aligned}
x_1 &= x_0-\frac{f(x_0)}{f'(x_0)}\\
f(0.3) &= 1.500-e^{0.300}=0.15014\\
f'(0.300) &= 5.000-1.34986=3.65014\\
x_1 &= 0.300-\frac{0.15014}{3.65014}\\
&= 0.300-0.04113=0.2589\\
x_2 &= x_1-\frac{f(x_1)}{f'(x_1)}\\
f(0.2589) &= 1.29434-e^{0.0.2589}\\
&= 1.29434-1.29546=-0.001130\\
f'(0.2589) &= 5.00-e^{0.2589}\\
&= 5.000-1.2956=3.70454\\
x_2 &= 0.2589-\frac{-0.001130}{3.70454}\\
&= 0.2589+0.00359=0.26245\\
x_3 &= x_2-\frac{f(x_2)}{f'(x_2)}\\
f(0.26245) &= 1.31226-e^{0.26245}\\
&= 1.31226-1.30011=0.01215\\
f'(0.26245) &= 5.00-e^{0.26245}\\
&= 5.000-1.30011=3.69989\\
x_3 &= 0.26245-\frac{0.01215}{3.69989}\\
&= 0.2589+0.00359=0.25917
\end{aligned}$$

We discontinue iteration at this point. The root is actually at $x=0.25917$ to five significant digits. Notice that the approximations oscillate around the correct value.

37. Solve the following equations by hand, using Newton's method. Verify your results using Excel or Mathematica:

a. $e^{-x}-0.3000x=0$. A rough graph indicates a root near $x=1$. We take $x_0=1.000$

$$\begin{aligned}
f &= e^{-x}-0.3000x\\
f' &= -e^{-x}-0.3000\\
x_1 &= x_0-\frac{f(x_0)}{f'(x_0)}\\
f(1.000) &= e^{-1.000}-0.3000=0.06788\\
f'(1.000) &= -e^{-1.000}-0.3000=-1.205\\
x_1 &= 1.000-\frac{0.06788}{-1.205}\\
&= 1.000+0.0563=1.0563
\end{aligned}$$

$$
\begin{aligned}
x_2 &= x_1 - \frac{f(x_1)}{f'(x_1)}\\
f(1.0563) &= e^{-1.0563} - (0.3000)(1.0563)\\
&= 0.3477 - 0.3169 = 0.03082\\
f'(1.0563) &= -e^{-1.0563} - (0.3000)(1.0563)\\
&= -0.3477 - 0.3169 = -0.6646\\
x_2 &= 1.0563 - \frac{0.03082}{-0.6646}\\
&= 1.0563 + 0.0464 = 1.10271\\
x_3 &= x_2 - \frac{f(x_2)}{f'(x_2)}\\
f(1.10271) &= e^{-1.10271} - (0.3000)(1.10271)\\
&= 0.33197 - 0.33081 = 0.001155\\
f'(1.10271) &= -e^{-1.0563} - (0.3000)(1.0563)\\
&= -0.33197 - 0.33081 = -0.66278\\
x_3 &= 1.10271 - \frac{0.001155}{-0.66278} = 1.1045
\end{aligned}
$$

To five significant digits, this is the correct answer.

b. $\sin(x)/x - 0.7500 = 0$. A graph indicates a root near $x = 1.25$. We take $x_0 = 1.25$.

$$
\sin(x)/x - 0.7500
$$

$$
f' = \frac{\cos(x)}{x} - \frac{\sin(x)}{x^2}
$$

$$
\begin{aligned}
x_1 &= x_0 - \frac{f(x_0)}{f'(x_0)}\\
f(1.25) &= \frac{\sin(1.25)}{1.25} - 0.7500 = 0.009188\\
f'(1.25) &= \frac{\cos(x)}{x} - \frac{\sin(x)}{x^2}\\
&= 0.25226 - 0.60735 = -0.35509\\
x_1 &= 1.25 - \frac{0.009188}{-0.35509}\\
&= 1.25 + 0.02587 = 1.2759\\
x_2 &= x_1 - \frac{f(x_1)}{f'(x_1)}\\
f(1.2759) &= \frac{\sin(1.2759)}{1.2759} - 0.7500\\
&= -0.00006335\\
f'(1.2759) &= \frac{\cos(x)}{x} - \frac{\sin(x)}{x^2}\\
&= 0.2278 - 0.58878 = -0.35997\\
x_1 &= 1.2759 - \frac{-0.00006335}{-0.35997}\\
&= 1.2759 - 0.000259 = 1.2756
\end{aligned}
$$

We stop iterating at this point. The correct answer to five significant digits is $x = 1.2757$

Integral Calculus

EXERCISES

Exercise 7.1. Find the maximum height for the particle in the preceding example.

We find the time of the maximum height by setting the first derivative of $z(t)$ equal to zero:

$$\frac{dz}{dt} = 0.00 \text{ m s}^{-1} = 10.00 \text{ m s}^{-1} - (9.80 \text{ m s}^{-2})t = 0$$

The time at which the maximum height is reached is

$$t = \frac{10.00 \text{ m s}^{-1}}{9.80 \text{ m s}^{-2}} = 1.020 \text{ s}$$

The position at this time is

$$\begin{aligned} z(t) &= (10.00 \text{ m s}^{-1})(1.020 \text{ s}) - \frac{(9.80 \text{ m s}^{-2})(1.020 \text{ s})^2}{2} \\ &= 5.204 \text{ m} \end{aligned}$$

Exercise 7.2. Find the function whose derivative is $-(10.00)e^{-5.00x}$ and whose value at $x = 0.00$ is 10.00.

The antiderivative of the given function is

$$F(x) = (2.00)e^{-5.00x} + C$$

where C is a constant.

$$\begin{aligned} F(0.00) &= 10.00 = (2.00)e^{0.00} + C \\ C &= 10.00 - 2.00 = 8.00 \\ F(x) &= (2.00)e^{-5.00x} + 8.00 \end{aligned}$$

Exercise 7.3. Evaluate the definite integral

$$\int_0^1 e^x \, dx.$$

The antiderivative function is $F = e^x$ so that the definite integral is

$$\begin{aligned} \int_0^1 e^x \, dx &= e^x|_0^1 = e^1 - e^0 = 2.71828 \cdots - 1 \\ &= 1.71828 \cdots \end{aligned}$$

Exercise 7.4. Find the area bounded by the curve representing $y = x^3$, the positive x axis, and the line $x = 3.000$.

$$\begin{aligned} \text{area} &= \int_{0.000}^{3.000} x^3 \, dx = \frac{1}{2}x^2\Big|_{0.000}^{3.000} = \frac{1}{2}(9.000 - 0.000) \\ &= 4.500 \end{aligned}$$

Exercise 7.5. Find the approximate value of the integral

$$\int_0^1 e^{-x^2} \, dx$$

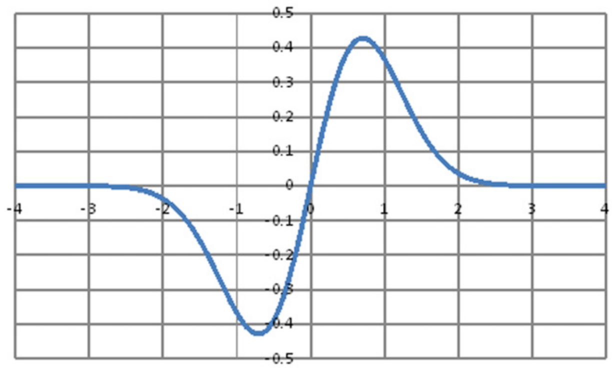
by making a graph of the integrand function and measuring an area.

We do not display the graph, but the correct value of the integral is 0.74682.

Exercise 7.6. Draw a rough graph of $f(x) = xe^{-x^2}$ and satisfy yourself that this is an odd function. Identify the area in this graph that is equal to the following integral and satisfy yourself that the integral vanishes:

$$\int_{-4}^{4} xe^{-x^2} \, dx = 0.$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00031-8



The area to the right of the origin is positive, and the area to the left of the origin is negative, and the two areas have the same magnitude.

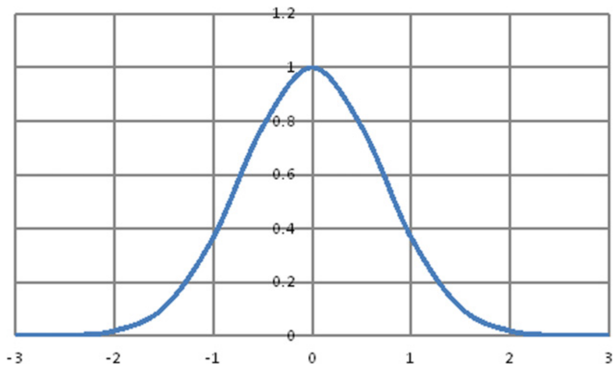
Exercise 7.7. Draw a rough graph of $f(x) = e^{-x^2}$. Satisfy yourself that this is an even function. Identify the area in the graph that is equal to the definite integral

$$I_1 = \int_{-3}^{3} e^{-x^2}\,\mathrm{d}x$$

and satisfy yourself that this integral is equal to twice the integral

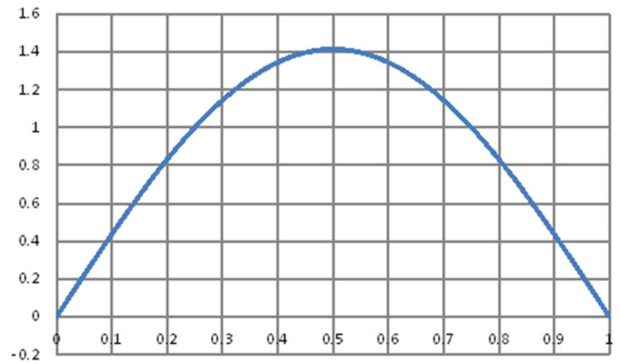
$$I_2 = \int_{0}^{3} e^{-x^2}\,\mathrm{d}x.$$

Here is the graph. The area to the left of the origin is equal to the area to the right of the origin. The value of the integrals are$I_1 = 1.4936$ and $I_2 = 0.7468$.

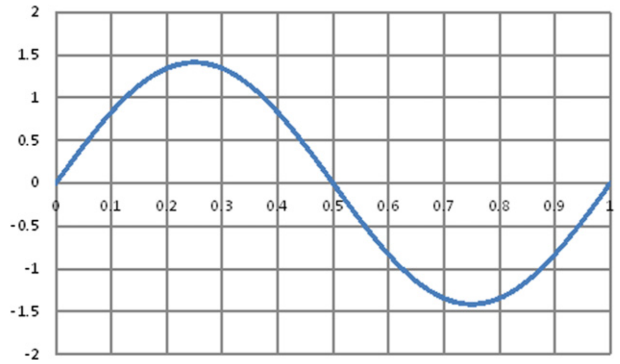


Exercise 7.8. **a.** By drawing rough graphs, satisfy yourself that ψ_1 is even about the center of the box. That is, $\psi_1(x) = \psi_1(a-x)$. Satisfy yourself that ψ_2 is odd about the center of box.

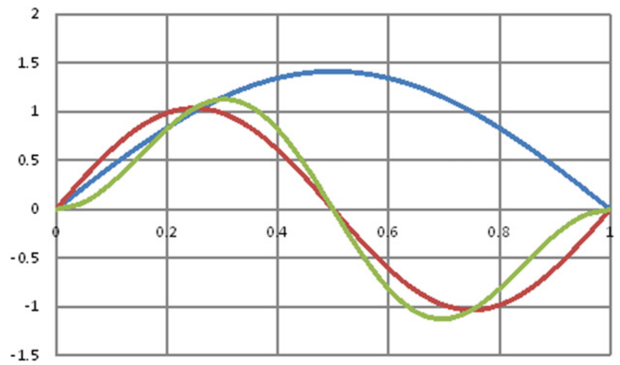
For the purpose of the graphs, we let $a = 1$. Here is a graph for ψ_1



Here is a graph for ψ_2:



b. Draw a rough graph of the product $\psi_1\psi_2$ and satisfy yourself that the integral of this product from $x = 0$ to $x = a$ vanishes. Here is graph of the two functions and their product:



Exercise 7.9. Using a table of indefinite integrals, find the definite integral.

$$\int_{0.000}^{3.000} \cosh(2x)\mathrm{d}x$$

$$\int_{0.000}^{3.000} \cosh(2x)\mathrm{d}x = \frac{1}{2}\int_{0.000}^{6.000} \cosh(y)\mathrm{d}y$$

$$= \frac{1}{2}\sinh(y)\Big|_{0.000}^{6.000} = \frac{1}{2}[\sinh(6.000) - \sinh(0.000)]$$

$$= \frac{1}{2}\sinh(6.000) = \frac{1}{4}[e^{6.000} - e^{-6.000}] = 100.8$$

Exercise 7.10. Determine whether each of the following improper integrals converges, and if so, determine its value:

a. $\int_0^1 \left(\frac{1}{x}\right) \mathrm{d}x$

$$\int_0^1 \left(\frac{1}{x}\right) \mathrm{d}x = \lim_{b\to 0} \ln(x)|_b^1 = 0 + \infty$$

This integral diverges since the integrand tends strongly toward infinity as x approaches $x = 0$.

b. $\int_0^\infty \left(\frac{1}{1+x}\right) \mathrm{d}x$

$$\int_0^\infty \left(\frac{1}{1+x}\right) \mathrm{d}x = \lim_{b\to\infty} \ln(1+x)|_0^b = \infty$$

This integral diverges since the integrand approaches zero too slowly as x becomes large.

Exercise 7.11. Evaluate the integral

$$\int_0^{\pi/2} e^{\sin(\theta)}\cos(\theta)\mathrm{d}\theta$$

without using a table of integrals. We let

$$\begin{aligned} y &= \sin(\theta) \\ \mathrm{d}y &= \cos(\theta)\mathrm{d}\theta \end{aligned}$$

$$\int_0^{\pi/2} e^{\sin(\theta)}\cos(\theta)\mathrm{d}\theta = \int_0^{\theta=\pi/2} e^y\,\mathrm{d}y = \int_0^{y=1} e^y\,\mathrm{d}y$$
$$= e^y|_0^1 = e - 1 = 1.7183$$

Exercise 7.12. Evaluate the integral

$$\int_0^\pi x^2\sin(x)\mathrm{d}x$$

without using a table. You will have to apply partial integration twice. For the first integration, we let $u(x) = x^2$ and $\sin(x)\mathrm{d}x = \mathrm{d}v$

$$\begin{aligned} \mathrm{d}u &= 2x\,\mathrm{d}x \\ v &= -\cos(x) \end{aligned}$$
$$\int_0^\pi x^2\sin(x)\mathrm{d}x = -x^2\cos(x)|_0^\pi + 2\int_0^\pi x\cos(x)\mathrm{d}x$$

For the second integration, we let $u(x) = x$ and $\cos(x)\mathrm{d}x = \mathrm{d}v$

$$\begin{aligned} \mathrm{d}u &= \mathrm{d}x \\ v &= \sin(x) \end{aligned}$$

$$\begin{aligned} \int_0^\pi x\cos(x)\mathrm{d}x &= x\sin(x)|_0^\pi - \int_0^\pi \sin(x)\mathrm{d}x \\ &= 0 + \cos(x)|_0^\pi = -2 \end{aligned}$$

$$\begin{aligned} \int_0^\pi x^2\sin(x)\mathrm{d}x &= -x^2\cos(x)|_0^\pi + 2\times(-2) \\ &= \pi^2 - 4 \end{aligned}$$

Exercise 7.13. Solve the simultaneous equations to obtain the result of the previous example.

$$\begin{aligned} A_1 + A_2 &= 6 \\ A_1 + 2A_2 &= -30 \end{aligned}$$

Subtract the first equation from the second equation:

$$A_2 = -36$$

Substitute this into the first equation

$$\begin{aligned} A_1 - 36 &= 6 \\ A_1 &= 42 \end{aligned}$$

Exercise 7.14. Use Mathematica to verify the partial fractions in the above example.

Solution not given.

Exercise 7.15. Show that the expressions for G and H are correct. Verify your result using Mathematica if it is available. Substitute the expressions for G and H into the equation

$$\begin{aligned} &\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)} \\ &= \left(\frac{1}{[\mathrm{A}]_0 - ax}\right)\left(\frac{1}{[\mathrm{B}]_0 - b[\mathrm{A}]_0/a}\right) \\ &\quad + \left(\frac{1}{[\mathrm{B}]_0 - bx}\right)\left(\frac{1}{[\mathrm{A}]_0 - a[\mathrm{B}]_0/b}.\right) \\ &= \left(\frac{1}{[\mathrm{A}]_0 - ax}\right)\left(\frac{([\mathrm{B}]_0 - bx)}{[\mathrm{B}]_0 - bx}\right)\left(\frac{a}{a[\mathrm{B}]_0 - b[\mathrm{A}]_0}\right) \\ &\quad + \left(\frac{[\mathrm{A}]_0 - ax}{[\mathrm{B}]_0 - bx}\right)\left(\frac{1}{[\mathrm{A}]_0 - ax}\right)\left(\frac{b}{b[\mathrm{A}]_0 - a[\mathrm{B}]_0}.\right) \\ &= \left(\frac{1}{[\mathrm{A}]_0 - ax}\right)\left(\frac{([\mathrm{B}]_0 - bx)}{[\mathrm{B}]_0 - bx}\right)\left(\frac{a}{a[\mathrm{B}]_0 - b[\mathrm{A}]_0}\right) \\ &\quad - \left(\frac{[\mathrm{A}]_0 - ax}{[\mathrm{B}]_0 - bx}\right)\left(\frac{1}{[\mathrm{A}]_0 - ax}\right)\left(\frac{b}{(a[\mathrm{B}]_0 - b[\mathrm{A}]_0)}\right) \\ &= \frac{a([\mathrm{B}]_0 - bx) - b([\mathrm{A}]_0 - ax)}{([\mathrm{B}]_0 - bx)([\mathrm{A}]_0 - ax)(a[\mathrm{B}]_0 - b[\mathrm{A}]_0)} \\ &= \frac{a[\mathrm{B}]_0 - abx - b[\mathrm{A}]_0 + abx}{([\mathrm{B}]_0 - bx)([\mathrm{A}]_0 - ax)(a[\mathrm{B}]_0 - b[\mathrm{A}]_0)} \\ &= \frac{1}{([\mathrm{B}]_0 - bx)([\mathrm{A}]_0 - ax)} \end{aligned}$$

Exercise 7.16. Using the trapezoidal approximation, evaluate the following integral, using five panels.

$$\int_{1.00}^{2.00} \cosh(x)\mathrm{d}x$$

We apply the definition of the hyperbolic cosine

$$\cosh(x) = \frac{1}{2}(e^x + e^{-x})$$

$$\begin{aligned}\int_{1.00}^{2.00} e^x\,\mathrm{d}x &\approx \left(\frac{e^{1.00}}{2} + e^{1.20} + e^{1.400}\right.\\ &\left.+e^{1.600} + e^{1.800} + \frac{e^{2.00}}{2}\right)\\ (0.200) &= 4.686\end{aligned}$$

$$\begin{aligned}\int_{1.00}^{2.00} e^{-x}\,\mathrm{d}x &\approx \left(\frac{e^{-1.00}}{2} + e^{-1.20} + e^{-1.400}\right.\\ &\left.+e^{-1.600} + e^{-1.800} + \frac{e^{-2.00}}{2}\right)\\ &\times(0.200) = 0.2333\end{aligned}$$

$$\int_{1.00}^{2.00} \cosh(x)\mathrm{d}x \approx \frac{4.6866 + 0.2333}{2} = 2.460$$

The correct value is 2.4517

Exercise 7.17. Apply Simpson's rule to the integral

$$\int_{10.00}^{20.00} x^2\,\mathrm{d}x$$

using two panels. Since the integrand curve is a parabola, your result should be exactly correct.

$$\begin{aligned}\int_{10.00}^{20.00} x^2\,\mathrm{d}x &\approx \frac{(f_0 + 4f_1 + f_n)\Delta x}{3}\\ &= \frac{1}{3}(10.00^2 + 4(15.00)^2 + 20.00^2)(5.00) = 2333.3\end{aligned}$$

This is correct to five significant digits.

Exercise 7.18. Using Simpson's rule, calculate the integral from $x = 0.00$ to $x = 1.20$ for the following values of the integrand.

x	0.00	0.20	0.40	0.60	0.80	1.00	1.20
$f(x)$	1.000	1.041	1.174	1.433	1.896	2.718	4.220

$$\begin{aligned}\int_{0.00}^{1.20} f(x)\mathrm{d}x &\approx \frac{1}{3}[1.000 + 4(1.041) + 2(1.174 + 4(1.433)\\ &+2(1.896) + 4(2.718) + 4.200)](0.20) \approx 2.142\end{aligned}$$

Exercise 7.19. Write Mathematica entries to obtain the following integrals:

a. $\int \cos^3(x)\mathrm{d}x$
b. $\int_1^2 e^{5x^2}\,\mathrm{d}x$

The correct values are

a.

$$\int \cos^3(x)\mathrm{d}x = \frac{3}{4}\sin x + \frac{1}{12}\sin 3x$$

b.

$$\int_1^2 e^{5x^2}\,\mathrm{d}x = 2.4917 \times 10^7$$

PROBLEMS

1. Find the indefinite integral without using a table:

a. $\int x\ln(x)\mathrm{d}x$

$$\begin{aligned}u(x) &= x\\ \mathrm{d}u/\mathrm{d}x &= 1\\ \ln(x) &= \mathrm{d}v/\mathrm{d}x\\ v &= x\ln(x) - x\\ \int x\ln(x)\mathrm{d}x &= x(x\ln(x) - x)\\ &-\int (x\ln(x) - x)\mathrm{d}x + C\\ 2\int x\ln(x)\mathrm{d}x &= x(x\ln(x) - x) + \int x\,\mathrm{d}x + C\\ &= x^2\ln(x) - x^2 + \frac{x^2}{2}\\ &= x^2\ln(x) - \frac{x^2}{2}\\ \int x\ln(x)\mathrm{d}x &= \left(\frac{1}{2}\right)x^2\ln(x) - \frac{x^2}{4}\end{aligned}$$

b. $\int x\sin^2(x)\mathrm{d}x$

$$\begin{aligned}\int x\sin^2(x)\mathrm{d}x &= \frac{1}{2}\int x[1 - \cos(2x)]\mathrm{d}x\\ &= \frac{1}{2}\int x\,\mathrm{d}x - \frac{1}{2}\int x\cos(2x)\mathrm{d}x\\ \int x\cos(2x)\mathrm{d}x &= \frac{1}{2}x\sin(2x)\\ &-\frac{1}{2}\int \sin(2x)\mathrm{d}x\\ &= \frac{1}{2}x\sin(2x) + \frac{1}{4}\sin(2x)\\ \int x\sin^2(x)\mathrm{d}x &= \frac{1}{4}x^2 - \frac{1}{4}x\sin(2x)\\ &-\frac{1}{8}\cos(2x)\end{aligned}$$

2. Find the indefinite integrals without using a table:

$\int \frac{1}{x(x-a)}\mathrm{d}x$

$$\begin{aligned}
\frac{1}{x(x-a)} &= \frac{A}{x} + \frac{B}{x-a} \\
1 &= A(x-a) + Bx \\
1 &= Ba \quad \text{if } x = a \\
B &= \frac{1}{a} \\
1 &= -Aa \quad \text{if } x = 0 \\
A &= -\frac{1}{a} \\
\frac{1}{x(x-a)} &= -\frac{1}{ax} + \frac{1}{a(x-a)} \\
\int \frac{1}{x(x-a)}\mathrm{d}x &= -\int \frac{1}{ax}\mathrm{d}x + \int \frac{1}{a(x-a)}\mathrm{d}x \\
&= -\frac{1}{a}\ln(x) + \frac{1}{a}\ln(x-a)
\end{aligned}$$

3. Evaluate the definite integrals, using a table of indefinite integrals

a. $\int_{1.000}^{2.000} \frac{\ln(3x)}{x}\mathrm{d}x$

$$\int_{1.00}^{2.00} \frac{\ln(3x)}{x}\mathrm{d}x = \frac{1}{2}[\ln(3x)]^2\Big|_1^2$$
$$= \frac{1}{2}\{[\ln(6.000)]^2 - [\ln(3.000)]\}^2 = 1.0017$$

b. $\int_{0.000}^{5.000} 4^x\,\mathrm{d}x$.

$$\begin{aligned}
\int_{0.000}^{5.000} 4^x\,\mathrm{d}x &= \frac{4^x}{\ln(4)}\Big|_{0.000}^{5.000} \\
&= \frac{1}{\ln(4)}\left(4^{5.000} - 4^{0.000}\right) \\
&= \frac{1}{1.38629}(1024.0 - 1.000) \\
&= 737.9
\end{aligned}$$

4. Evaluate the definite integral: $\int_0^{2\pi} \sin^2(x)\mathrm{d}x$

$$\int_0^{2\pi} \sin^2(x)\mathrm{d}x = \left(\frac{x}{2} - \frac{\sin(2x)}{4}\right)\Big|_0^{2\pi} = \pi$$

5. Evaluate the definite integral: $\int_2^4 \frac{1}{x\ln(x)}\mathrm{d}x$

$$\begin{aligned}
\int_2^4 \frac{1}{x\ln(x)}\mathrm{d}x &= \ln(\ln(|(x)|)|_2^4 = \ln(\ln(4))) \\
&\quad - \ln(\ln 2)) \\
&= \ln(1.38629) - \ln(0.69315) \\
&= 0.32663 + 0.36651 = 0.69314
\end{aligned}$$

6. Evaluate the definite integral: $\int_0^{\pi/2} \sin(x)\cos(x)\mathrm{d}x$

$$\int_0^{\pi/2} \sin(x)\cos(x)\mathrm{d}x = \frac{\sin^2(x)}{2}\Big|_0^{\pi/2} = \frac{1}{2}(1-0) = \frac{1}{2}$$

7. Evaluate the definite integral: $\int_1^{10} x\ln(x)\mathrm{d}x$

$$\begin{aligned}
\int_1^{10} x\ln(x)\mathrm{d}x &= \left(\frac{x^2}{2}\ln(x) - \frac{x^2}{4}\right)\Big|_1^{10} \\
&= 50\ln(10) - \frac{100}{4} + \frac{1}{4} \\
&= 50\ln(10) - \frac{99}{4} = 90.38
\end{aligned}$$

8. Evaluate the definite integral: $\int_0^{\pi/2} \sin(x)\cos^2(x)\mathrm{d}x$. Let $u = \cos(x), \mathrm{d}u = -\sin(x)\mathrm{d}x$

$$\begin{aligned}
\int_0^{\pi/2} \sin(x)\cos^2(x)\mathrm{d}x &= -\int_1^0 u^2\,\mathrm{d}u \\
&= -\frac{1}{3}u^3\Big|_1^0 = \frac{1}{3}
\end{aligned}$$

9. Evaluate the definite integral: $\int_0^{\pi/2} x\sin(x^2)\,\mathrm{d}x = \frac{1}{2} - \frac{1}{2}\cos\frac{1}{4}\pi^2$. $\int x\sin(x^2)\mathrm{d}x = -\frac{1}{2}\cos x^2$.

$$\begin{aligned}
\int_0^{\pi/2} x\sin(x^2)\mathrm{d}x &= \frac{1}{2}\int_0^{\pi^2/4} \sin(u)\mathrm{d}u \\
&= -\frac{1}{2}\cos(u)\Big|_0^{\pi^2/4} \\
&= -\frac{1}{2}\cos(\pi^2/4) + \frac{1}{2} = -\frac{1}{2}(-0.78121) + \frac{1}{2} \\
&= 0.89061
\end{aligned}$$

10. Evaluate the definite integral:
$\int_0^{\pi/2} x\sin(x^2)\cos(x^2)\mathrm{d}x = \frac{1}{8} - \frac{1}{8}\cos\frac{1}{2}\pi^2$

$$\begin{aligned}\int_0^{\pi/2} & x\sin(x^2)\cos(x^2)\mathrm{d}x \\ &= \frac{1}{2}\int_0^{\pi^2/4}\sin(u)\cos(u)\mathrm{d}u \\ &= \frac{1}{4}\int_0^{\pi^2/4}\sin(2u)\mathrm{d}u \\ &= -\frac{1}{8}\cos(2u)\Big|_0^{\pi^2/4} = -\frac{1}{8}\cos\left(\frac{\pi^2}{2}\right) + \frac{1}{8} \\ &= -\frac{1}{8}(0.22058) + \frac{1}{8} = 0.9743\end{aligned}$$

11. Find the following area by computing the values of a definite integral: The area bounded by the straight line $y = 2x + 3$, the x axis, the line $x = 1$, and the line $x = 4$.

$$\begin{aligned}\text{area} &= \int_1^4 (2x+3)\mathrm{d}x = (x^2 + 3x)|_1^4 \\ &= 16 + 12 - 1 - 3 = 24\end{aligned}$$

12. Find the following area by computing the values of a definite integral: The area bounded by the parabola $y = 4 - x^2$ and the x axis. You will have to find the limits of integration. The integrand vanishes when$x = -2$ or $x = 2$ so these are the limits.

$$\begin{aligned}\text{area} &= \int_{-2}^{2}(4 - x^2)\mathrm{d}x = \left(4x - \frac{1}{3}x^3\right)\Big|_{-2}^{2} \\ &= 8 - \frac{8}{3} - (-8) + \frac{-8}{3} \\ &= 16 - \frac{16}{3} = \frac{32}{3} = 10.667\end{aligned}$$

13. Determine whether each of the following improper integrals converges, and if so, determine its value:

a. $\int_0^\infty \frac{1}{x^3}\mathrm{d}x$

$$\int_0^\infty \frac{1}{x^3}\mathrm{d}x = -\frac{1}{2x^2}\Big|_0^\infty = 0 + \infty \quad \text{(diverges)}$$

b. $\int_{-\infty}^0 e^x\,\mathrm{d}x$

$$\int_{-\infty}^0 e^x\,\mathrm{d}x = e^x|_{-\infty}^0 = 1 \quad \text{(converges)}$$

14. Determine whether the following improper integrals converge. Evaluate the convergent integrals.

a. $\int_1^\infty \left(\frac{1}{x^2}\right)\mathrm{d}x$ converges

$$\int_1^\infty \left(\frac{1}{x^2}\right)\mathrm{d}x = -\frac{1}{x}\Big|_1^\infty = -0 + 1 = 1$$

b. $\int_1^{\pi/2} \tan(x)\mathrm{d}x$. diverges

$$\begin{aligned}\int_1^{\pi/2} \tan(x)\mathrm{d}x &= -\ln[\cos(x)|]|_1^{\pi/2} \\ &= -\lim_{x\to\pi/2}\ln[\cos(x) + \ln[\cos(1)] = -\infty\end{aligned}$$

15. Determine whether the following improper integrals converge. Evaluate the convergent integrals

a. $\int_0^1 \frac{1}{x\ln(x)}\mathrm{d}x = -\infty$

b. $\int_1^\infty \left(\frac{1}{x}\right)\mathrm{d}x = \infty$

16. Determine whether the following improper integrals converge. Evaluate the convergent integrals $\int_0^\pi \tan(x)\mathrm{d}x$

a. $\int_0^{\pi/2} \tan(x)\mathrm{d}x$

b. $\int_0^1 \left(\frac{1}{x}\right)\mathrm{d}x$

17. Determine whether the following improper integrals converge. Evaluate the convergent integrals.

a. $\int_0^\infty \sin(x)\mathrm{d}x$ diverges, The integrand continues to oscillate as x increases,

b. $\int_{-\pi/2}^{\pi/2} \tan(x)\mathrm{d}x$

$$\begin{aligned}\int_{-\pi/2}^{\pi/2} \tan(x)\mathrm{d}x &= \lim_{u\to\pi/2}\ln(|\cos(u)|)\Big|_{-u}^{u} \\ &= \lim_{u\to\pi/2}[\ln(\cos(u)) - \ln(\cos(u))] = 0\end{aligned}$$

Since the cosine is an even function, the two terms are canceled before taking the limit, so that the result vanishes.

18. Approximate the integral

$$\int_0^\infty e^{-x^2}\,\mathrm{d}x$$

using Simpson's rule. You will have to take a finite upper limit, choosing a value large enough so that the error caused by using the wrong limit is negligible. The correct answer is $\sqrt{\pi}/2 = 0.886226926\cdots$. With an upper limit of 4.00 and $\Delta x = 0.100$ the result was 0.886226912, which is correct to seven significant digits.

19. Using Simpson's rule, evaluate erf(2):

$$\mathrm{erf}(2) = \frac{2}{\sqrt{\pi}}\int_0^{2.000} e^{-t^2}\,\mathrm{d}t$$

Compare your answer with the correct value from a more extended table than the table in Appendix G, $erf(2.000) = 0.995322265$. With $\Delta x = 0.0500$, the result from Simpson's rule was 0.997100808. With $\Delta x = 0.100$, the result from Simpson's rule was 0.99541241.

20. Find the integral: $\int \sin[x(x+1)](2x+1)\mathrm{d}x$. Let $u = 2^2 + x$; $\mathrm{d}u = (3x+1)\mathrm{d}x$

$$\int \sin[x(x+1)](2x+1)\mathrm{d}x = \int \sin(u)\mathrm{d}u$$
$$= -\cos(u) = -\cos(x^2+x)$$

21. Find the integral:

$$\int x\ln(x^2)\mathrm{d}x = \frac{1}{2}\int \ln(u)\mathrm{d}u$$
$$= \frac{1}{2}[u\ln(u) - u] = \frac{1}{2}x^2\ln(x^2) - \frac{1}{2}x^2$$

22. When a gas expands reversibly, the work that it does on its surroundings is given by the integral

$$w_{surr} = \int_{V_1}^{V_2} P\,\mathrm{d}V,$$

where V_1 is the initial volume, V_2 the final volume, and P the pressure of the gas. Certain nonideal gases are described by the van der Waals equation of state,

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

where V is the volume, n is the amount of gas in moles, T is the temperature on the Kelvin scale, and a and b are constants. R is usually taken to be the ideal gas constant, 8.3145 J K^{-1} mol^{-1}.

a. Obtain a formula for the work done on the surroundings if 1.000 mol of such a gas expands reversibly at constant temperature from a volume V_1 to a volume V_2.

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

$$w_{surr} = \int_{V_1}^{V_2} P\,\mathrm{d}V = \int_{V_1}^{V_2}\left[\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right]\mathrm{d}V$$
$$= nRT\ln\left(\frac{V_2 - nb}{V_1 - nb}\right) + n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

b. If $T = 298.15$ K, $V_1 = 1.00$ l $(1.000 \times 10^{-3}\ \mathrm{m}^3)$, and $V_2 = 100.0$ l $= 0.100\ \mathrm{m}^3$, find the value of the work done for 1.000 mol of CO_2, which has $a = 0.3640$ Pa m^6 mol^{-2}, and $b = 4.267 \times 10^{-5}$ m^3 mol^{-1}. The ideal gas constant, $R = 8.3145$ J K^{-1} mol^{-1}.

$$w_{surr} = (1.000\ \mathrm{mol})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})$$
$$\times (298.15\ \mathrm{K})$$
$$\times \ln\left(\frac{0.100\ \mathrm{m}^3 - 4.267 \times 10^{-5}\ \mathrm{m}^3}{0.00100\ \mathrm{m}^3 - 4.267 \times 10^{-5}\ \mathrm{m}^3}\right)$$
$$+ (0.3640\ \mathrm{Pa\ m}^6)$$
$$\times \left(\frac{1}{0.100\ \mathrm{m}^3} - \frac{1}{0.00100\ \mathrm{m}^3}\right)$$
$$= 11523\ \mathrm{J} - 360\ \mathrm{Pa\ m}^3$$
$$= 11523\ \mathrm{J} - 360\ \mathrm{J} = 11163\ \mathrm{J}$$

c. Calculate the work done in the process of part b if the gas is assumed to be ideal.

$$w_{surr} = \int_{V_1}^{V_2} P\,\mathrm{d}V = \int_{V_1}^{V_2} \frac{nRT}{V}\mathrm{d}V$$
$$= nRT\ln\left(\frac{V_2}{V_1}\right)$$
$$= (1.000\ \mathrm{mol})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})$$
$$\times (298.15\ \mathrm{K})\ln\left(\frac{0.100\ \mathrm{m}^3}{0.00100\ \mathrm{m}^3}\right)$$
$$-11416\ \mathrm{J}$$

23. The entropy change to bring a sample from 0 K (absolute zero) to a given state is called the absolute entropy of the sample in that state.

$$S_m(T') = \int_0^{T'} \frac{C_{P,m}}{T}\mathrm{d}T$$

where $S_m(T')$ is the absolute molar entropy at temperature T', $C_{P,m}$ is the molar heat capacity at constant pressure, and T is the absolute temperature. Using Simpson's rule, calculate the absolute entropy of 1.000 mol of solid silver at 270 K. For the region 0 K to 30 K, use the approximate relation

$$C_P = aT^3,$$

where a is a constant that you can evaluate from the value of C_P at 30 K. For the region 30 K to 270 K, use the following data:[1]

[1] Meads. Forsythe, and Giaque, *J. Am. Chem. Soc.* **63**, 1902 (1941).

T/K	C_P/J K^{-1} mol^{-1}	T/K	C_P/J K^{-1} mol^{-1}
30	4.77	170	23.61
50	11.65	190	24.09
70	16.33	210	24.42
90	19.13	230	24.73
110	20.96	250	25.03
130	22.13	270	25.31
150	22.97		

We divide the integral into two parts, one from $t = 0$ K to $T = 30$ K, and one from 30 K to 270 K.

$$a = \frac{4.77 \text{ J K}^{-1} \text{ mol}^{-1}}{(30 \text{ K})^3} = 1.77 \times 10^{-4}$$

$$\begin{aligned} S_m(30 \text{ K}) &= \int_0^{30 \text{ K}} \frac{C_{P,m}}{T} \mathrm{d}T = \int_0^{30 \text{ K}} \frac{a}{T^4} \mathrm{d}T \\ &= \frac{1}{3} \frac{a}{T^3} = \frac{1}{3} C_{P.m}(30 \text{ K}) \\ &= 1.59 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} S_m(270 \text{ K}) &= 1.59 \text{ J K}^{-1} \text{ mol}^{-1} \\ &\quad + \int_{30 \text{ K}}^{270 \text{ K}} \frac{C_{P,m}}{T} \mathrm{d}T \end{aligned}$$

The second integral is evaluated using Simpson's rule. The result is of this integration is 38.397 J K^{-1} mol^{-1} so that

$$\begin{aligned} S_m(270 \text{ K}) &= 1.59 \text{ J K}^{-1} \text{ mol}^{-1} + 38.40 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 39.99 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

24. Use Simpson's rule with at least 10 panels to evaluate the following definite integrals. Use Mathematica to check your results. $\int_0^2 e^{-3x^3}\, \mathrm{d}x$ Using Simpson's rule with 20 panels, the result was 0.61917. The correct value is 0.61916.

25. Use Simpson's rule with at least 4 panels to evaluate the following definite integral. Use Mathematica to check your results.

$$\int_1^3 e^{x^2}\, \mathrm{d}x$$

With 20 panels, the result was 1444.2. The correct value is 1443.1.

Chapter 8

Differential Calculus with Several Independent Variables

EXERCISES

Exercise 8.1. The volume of a right circular cylinder is given by

$$V = \pi r^2 h,$$

where r is the radius and h the height. Calculate the percentage error in the volume if the radius and the height are measured and a 1.00% error is made in each measurement in the same direction. Use the formula for the differential, and also direct substitution into the formula for the volume, and compare the two answers.

$$\begin{aligned}
\Delta V &\approx \left(\frac{\partial V}{\partial r}\right)_h \Delta r + \left(\frac{\partial V}{\partial h}\right)_r \Delta h \\
&\approx 2\pi r h \Delta r + \pi r^2 \Delta h \\
\frac{\Delta V}{V} &\approx \frac{2\pi r h \Delta r}{\pi r^2 h} + \frac{\pi r^2 \Delta h}{\pi r^2 h} = \frac{2\Delta r}{r} + \frac{\Delta h}{h} \\
&= 2(0.0100) + 0.0100 = 0.0300
\end{aligned}$$

The estimated percent error is 3%. We find the actual percent error:

$$\begin{aligned}
\frac{V_2 - V_1}{V_1} &= \frac{\pi r^2 (1.0100)^2 h(1.0100)}{\pi r^2 h} - \frac{\pi r^2 h}{\pi r^2 h} \\
&= (1.0100)^3 - 1 = 1.03030 - 1 = .03030 \\
\text{percent error} &= 3.03\%
\end{aligned}$$

Exercise 8.2. Complete the following equations.

a. $\left(\frac{\partial H}{\partial T}\right)_{P,n} = \left(\frac{\partial H}{\partial T}\right)_{V,n} + ?$

$$\left(\frac{\partial H}{\partial T}\right)_{P,n} = \left(\frac{\partial H}{\partial T}\right)_{V,n} + \left(\frac{\partial H}{\partial V}\right)_{t,n} \left(\frac{\partial V}{\partial T}\right)_{P,n}$$

b. $\left(\frac{\partial z}{\partial u}\right)_{x,y} = \left(\frac{\partial z}{\partial u}\right)_{x,w} + ?$

$$\left(\frac{\partial z}{\partial u}\right)_{x,y} = \left(\frac{\partial z}{\partial u}\right)_{x,w} + \left(\frac{\partial z}{\partial w}\right)_{x,u} \left(\frac{\partial w}{\partial u}\right)_{x,y}$$

c. Apply the equation of part b if $z = z(x,y,u) = \cos(x) + y/u$ and $w = y/u$.

$$\left(\frac{\partial z}{\partial u}\right)_{x,y} = -\frac{y}{u^2}$$

$$\begin{aligned}
z(x,u,w) &= \cos(x) + w \\
\left(\frac{\partial z}{\partial w}\right)_{x,u} &= 1 \\
w(x,y,u) &= -\cos(x) + z \\
\left(\frac{\partial w}{\partial u}\right)_{x,y} &= \left(\frac{\partial z}{\partial u}\right)_{x,y} = -\frac{y}{u^2}
\end{aligned}$$

$$\left(\frac{\partial z}{\partial w}\right)_{x,u} \left(\frac{\partial w}{\partial u}\right)_{x,y} = 1\left(-\frac{y}{u^2}\right) = \left(\frac{\partial z}{\partial u}\right)_{x,y}$$

Exercise 8.3. Show that the reciprocal identity is satisfied by $(\partial z/\partial x)$ and $(\partial z/\partial z)_y$ if

$$z = \sin\left(\frac{x}{y}\right) \quad \text{and} \quad x = y\sin^{-1}(z) = y\arcsin(z).$$

From the table of derivatives

$$\begin{aligned}
\left(\frac{\partial z}{\partial x}\right)_y &= \frac{1}{y}\cos\left(\frac{x}{y}\right) \\
\left(\frac{\partial x}{\partial z}\right)_y &= y\frac{1}{\sqrt{1-z^2}} = \frac{y}{\sqrt{1-\sin^2\left(\frac{x}{y}\right)}} = \frac{y}{\cos\left(\frac{x}{y}\right)}
\end{aligned}$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00032-X

where we have used the identity

$$\sin^2(\alpha) + \cos^2(\alpha) = 1$$

Exercise 8.4. Show by differentiation that $(\partial^2 z/\partial y\partial x) = (\partial^2 z/\partial x\partial y)$ if

$$z = e^{xy}\sin(x).$$

$$\begin{aligned}\frac{\partial^2 z}{\partial y\partial x} &= \frac{\partial}{\partial y}[ye^{xy}\sin(x) + e^{xy}\cos(x)] \\ &= \frac{\partial}{\partial y}\{e^{xy}[y\sin(x) + \cos(x)]\} \\ &= e^{xy}[xy\sin(x) + x\cos(x)] + e^{xy}\sin(x)]\end{aligned}$$

$$\begin{aligned}\frac{\partial^2 z}{\partial x\partial y} &= \frac{\partial}{\partial x}xe^{xy}\sin(x) \\ &= e^{xy}\sin(x) + xye^{xy}\sin(x) + xe^{xy}\cos(x) \\ &= e^{xy}[xy\sin(x) + x\cos(x)] + e^{xy}\sin(x)]\end{aligned}$$

Exercise 8.5. Using the mnemonic device, write three additional Maxwell relations.

$$\begin{aligned}\left(\frac{\partial T}{\partial P}\right)_{S,n} &= \left(\frac{\partial V}{\partial S}\right)_{V,n} \\ \left(\frac{\partial S}{\partial P}\right)_{T,n} &= -\left(\frac{\partial V}{\partial T}\right)_{P,n} \\ \left(\frac{\partial S}{\partial V}\right)_{T,n} &= \left(\frac{\partial P}{\partial T}\right)_{V,n}\end{aligned}$$

Exercise 8.6. For the function $y = x^2/z$, show that the cycle rule is valid.

$$\begin{aligned}\left(\frac{\partial y}{\partial x}\right)_z &= \frac{2x}{z} \\ \left(\frac{\partial x}{\partial z}\right)_y &= \left(\frac{\partial[(yz)^{1/2}]}{\partial z}\right)_y = \frac{1}{2}y^{1/2}z^{-1/2} \\ \left(\frac{\partial z}{\partial y}\right)_x &= -\frac{x^2}{y^2}\end{aligned}$$

$$\begin{aligned}\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x &= \left(\frac{2x}{z}\right)\left(\frac{1}{2}y^{1/2}z^{-1/2}\right) \\ &\quad\times\left(-\frac{x^2}{y^2}\right) = -\frac{x^3}{z^{3/2}y^{3/2}} \\ &= -\frac{z^{3/2}y^{3/2}}{z^{3/2}y^{3/2}} = -1\end{aligned}$$

Exercise 8.7. Show that if $z = ax^2 + bu\sin(y)$ and $x = uvy$ then the chain rule is valid.

$$\begin{aligned}z(u,v,y) &= a(uvy)^2 + bu\sin(y) \\ \left(\frac{\partial z}{\partial y}\right)_{u,v} &= 2au^2v^2y + bu\cos(y) \\ z(u,v,x) &= ax^2 + bu\sin\left(\frac{x}{uv}\right) \\ \left(\frac{\partial z}{\partial x}\right)_{u,v} &= 2ax + \frac{bu}{uv}\cos\left(\frac{x}{uv}\right) \\ \left(\frac{\partial x}{\partial y}\right)_{u,v} &= uv \\ \left(\frac{\partial z}{\partial x}\right)_{u,v}\left(\frac{\partial x}{\partial y}\right)_{u,v} &= \left[2ax + \frac{bu}{uv}\cos\left(\frac{x}{uv}\right)\right]uv \\ &= 2auvx + bu\cos(y) \\ &= 2au^2v^2y + bu\cos(y)\end{aligned}$$

Exercise 8.8. Determine whether the following differential is exact:

$$du = (2ax + by^2)dx + (bxy)dy$$

$$\begin{aligned}\left(\frac{\partial(2ax + by^2)}{\partial y}\right)_x &= 2by \\ \left(\frac{\partial(bxy)}{\partial x}\right)_y &= by\end{aligned}$$

The differential is not exact.

Exercise 8.9. Show that the following is not an exact differential $du = (2y)dx + (x)dy + \cos(z)dz$.

$$\begin{aligned}\left(\frac{\partial(2y)}{\partial y}\right)_x &= 2 \\ \left(\frac{\partial x}{\partial x}\right)_y &= 1\end{aligned}$$

There is no need to test the other two relations.

Exercise 8.10. The thermodynamic energy of a monatomic ideal gas is given by

$$U = \frac{3nRT}{2}$$

Find the partial derivatives and write the expression for dU using T, V, and n as independent variables. Show that your differential is exact.

$$\begin{aligned}\left(\frac{\partial U}{\partial T}\right)_{V,n} &= \frac{3nR}{2} \\ \left(\frac{\partial U}{\partial V}\right)_{T,n} &= 0 \\ \left(\frac{\partial U}{\partial n}\right)_{V,n} &= \frac{3RT}{2}\end{aligned}$$

$$\begin{aligned}
\mathrm{d}U &= \left(\frac{3nR}{2}\right)\mathrm{d}T + (0)\mathrm{d}V + \left(\frac{3RT}{2}\right)\mathrm{d}n\\
\left(\frac{\partial^2 U}{\partial V \partial T}\right)_n &= 0\\
\left(\frac{\partial^2 U}{\partial T \partial V}\right)_n &= 0\\
\left(\frac{\partial^2 U}{\partial V \partial n}\right)_T &= 0\\
\left(\frac{\partial^2 U}{\partial n \partial V}\right)_T &= 0\\
\left(\frac{\partial^2 U}{\partial n \partial T}\right)_V &= \frac{3R}{2}\\
\left(\frac{\partial^2 U}{\partial T \partial n}\right)_V &= \frac{3R}{2}
\end{aligned}$$

Exercise 8.11. Show that the differential

$$(1+x)\mathrm{d}x + \left[\frac{x\ln(x)}{y} + \frac{x^2}{y}\right]\mathrm{d}y$$

is inexact, and that y/x is an integrating factor.

$$\begin{aligned}
\frac{\partial}{\partial y}(1+x) &= 0\\
\frac{\partial}{\partial x}\left[\frac{x\ln(x)}{y} + \frac{x^2}{y}\right] &= \frac{\ln(x)}{y} + \frac{1}{y} + \frac{2x}{y} \neq 0
\end{aligned}$$

The new differential is

$$\frac{y(1+x)}{x}\mathrm{d}x + [\ln(x) + x]\mathrm{d}y$$
$$\left(\frac{y}{x} + y\right)\mathrm{d}x + [\ln(x) + x]\mathrm{d}y$$

$$\begin{aligned}
\frac{\partial}{\partial y}\left(\frac{y}{x} + 1\right) &= \frac{1}{x} + 1\\
\frac{\partial}{\partial x}[\ln(x) + x] &= \frac{1}{x} + 1
\end{aligned}$$

Exercise 8.12. Evaluate D at the point (0,0) for the function of the previous example and establish that the point is a local maximum.

$$\begin{aligned}
\left(\frac{\partial f}{\partial x}\right)_y &= -2xe^{-x^2-y^2}\\
\left(\frac{\partial^2 f}{\partial x^2}\right)_y &= -2e^{-x^2-y^2} - 2xe^{-x^2-y^2}(-2x)\\
&= (4x^2-2)e^{-x^2-y^2}\\
\left(\frac{\partial f}{\partial y}\right)_x &= -2ye^{-x^2-y^2} = 0\\
\left(\frac{\partial^2 f}{\partial y^2}\right)_x &= -2e^{-x^2-y^2} - 2ye^{-x^2-y^2}(-2y)\\
&= (4y^2-2)e^{-x^2-y^2}\\
\left(\frac{\partial^2 f}{\partial x \partial y}\right) &= -2ye^{-x^2-y^2}(-2x) = 4xye^{-x^2-y^2}
\end{aligned}$$

At (0,0)

$$\begin{aligned}
D &= (-2)(-2) - 0 = 4\\
\left(\frac{\partial^2 f}{\partial x^2}\right)_y &= -2
\end{aligned}$$

Since $D \succ 0$ and $(\partial^2 f/\partial x^2)_y \prec 0$, we have a local maximum.

Exercise 8.13. **a.** Find the local minimum in the function

$$f(x,y) = x^2 + y^2 + 2x$$

At a relative extremum

$$\begin{aligned}
\left(\frac{\partial f}{\partial x}\right)_y &= 2x+2\\
\left(\frac{\partial^2 f}{\partial x^2}\right)_y &= 2\\
\left(\frac{\partial f}{\partial y}\right)_x &= 2y\\
\left(\frac{\partial^2 f}{\partial y^2}\right)_x &= 2\\
\left(\frac{\partial^2 f}{\partial x \partial y}\right) &= 0
\end{aligned}$$

At the extremum

$$\begin{aligned}
2x+2 &= 0\\
2y &= 0
\end{aligned}$$

This corresponds to $x = -1, y = 0$.

$$D = \left(\frac{\partial^2 f}{\partial x^2}\right)\left(\frac{\partial^2 f}{\partial y^2}\right) - \left(\frac{\partial^2 f}{\partial x \partial y}\right)^2 = (2)(2) - 0 = 4$$

This point, $(-1,0)$, corresponds to a local minimum. The value of the function at this point is

$$f(-1,0) = (-1)^2 + 2(-1) = -1$$

b. Find the constrained minimum subject to the constraint

$$x + y = 0.$$

On the constraint, $x = -y$. Substitute the constraint into the function. Call the constrained function $g(x,y)$.

$$\begin{aligned}
g(x,y) &= x^2 + (-x)^2 + 2x = 2x^2 + 2x\\
\frac{\partial g}{\partial x} &= 4x + 2
\end{aligned}$$

At the constrained relative minimum

$$x = -1/2, \quad y = 1/2$$

The value of the function at this point is

$$f(-1/2,1/2) = \frac{1}{4} + \frac{1}{4} - 2(1/2) = -\frac{1}{2}$$

c. Find the constrained minimum using the method of Lagrange.

The constraint can be written

$$g(x,y) = x + y = 0$$

so that

$$u(x,y) = x^2 + y^2 + 2x + \lambda(x+y)$$

The equations to be solved are

$$\left(\frac{\partial u}{\partial x}\right)_y = 2x + 2 + \lambda = 0$$
$$\left(\frac{\partial u}{\partial y}\right)_x = 2y + \lambda = 0$$

Solve the second equation for λ:

$$\lambda = -2y$$

Substitute this into the first equation:

$$2x + 2 - 2y = 0$$

We know from the constraint that $y = -x$ so that

$$4x + 2 = 0$$
$$x = -\frac{1}{2}$$
$$y = \frac{1}{2}$$

The value of the function is

$$f\left(-\frac{1}{2},\frac{1}{2}\right) = \frac{1}{4} + \frac{1}{4} - 1 = -\frac{1}{2}$$

Exercise 8.14. Find the minimum of the previous example without using the method of Lagrange. We eliminate y and z from the equation by using the constraints:

$$f = x^2 + 1 + 4 = x^2 + 5$$

The minimum is found by differentiating:

$$\frac{\partial f}{\partial x} = 2x = 0$$

The solution is

$$x = 0, \quad y = 1, \quad z = 2$$

Exercise 8.15. Find the gradient of the function

$$g(x,y,z) = ax^3 + ye^{bz},$$

where a and b are constants.

$$\nabla g = \mathbf{i}\left(\frac{\partial g}{\partial y}\right) + \mathbf{j}\left(\frac{\partial g}{\partial y}\right) + \mathbf{k}\left(\frac{\partial g}{\partial z}\right) = \mathbf{i}3ax^2 + \mathbf{j}e^{bz} + \mathbf{k}bye^{bz}$$

Exercise 8.16. The average distance from the center of the sun to the center of the earth is 1.495×10^{11} m. The mass of the earth is 5.983×10^{24} kg, and the mass of the sun is greater than the mass of the earth by a factor of 332958. Find the magnitude of the force exerted on the earth by the sun and the magnitude of the force exerted on the sun by the earth.

The magnitude of the force on the earth due to the sun is the same as the magnitude of the force on the sun due to the earth:

$$\begin{aligned} F &= Gm_s m_e \frac{|\mathbf{r}|}{r^3} = Gm_s m_e \frac{1}{r^2} \\ &= \frac{(6.673\times 10^{-11}\ \mathrm{m^3\ s^{-2}\ kg^{-1}})(5.983\times 10^{24}\ \mathrm{kg})^2(332958)}{(1.495\times 10^{11}\ \mathrm{m})^2} \\ &= 3.558\times 10^{22}\ \mathrm{kg\ m^2\ s^{-2}} = 3.558\times 10^{22}\ \mathrm{J} \end{aligned}$$

Exercise 8.17. Find $\nabla \cdot \mathbf{r}$ if

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z.$$
$$\nabla \cdot \mathbf{r} = \left(\frac{\partial x}{\partial x}\right) + \left(\frac{\partial y}{\partial y}\right) + \left(\frac{\partial z}{\partial z}\right) = 3$$

Exercise 8.18. Find $\nabla \times \mathbf{r}$ where

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z.$$

Explain your result.

$$\begin{aligned} \nabla\times\mathbf{r} &= \mathbf{i}\left(\frac{\partial z}{\partial y} - \frac{\partial y}{\partial z}\right) + \mathbf{j}\left(\frac{\partial x}{\partial z} - \frac{\partial z}{\partial x}\right) + \mathbf{k}\left(\frac{\partial y}{\partial x} - \frac{\partial x}{\partial y}\right) \\ &= 0 \end{aligned}$$

The interpretation of this result is that the vector r has no rotational component.

Exercise 8.19. Find the Laplacian of the function $f = \exp(x^2+y^2+z^2) = e^{x^2}e^{y^2}e^{z^2}$.

$$\begin{aligned} \nabla^2 f &= \left(\frac{\partial}{\partial x}2xe^{x^2}\right)e^{y^2}e^{z^2} + \left(\frac{\partial}{\partial y}2ye^{y^2}\right)e^{x^2}e^{z^2} \\ &\quad + \left(\frac{\partial}{\partial z}2ze^{z^2}\right)e^{x^2}e^{y^2} \\ &= (2e^{x^2} + 4x^2e^{x^2})e^{y^2}e^{z^2} + (2e^{y^2} + 4y^2e^{y^2})e^{x^2}e^{z^2} \\ &\quad + (2e^{z^2} + 4z^2e^{z^2})e^{x^2}e^{y^2} \\ &= [6 + 4(x^2+y^2+z^2)]e^{x^2}e^{y^2}e^{z^2} \end{aligned}$$

Exercise 8.20. Show that $\nabla \times \nabla f = 0$ if f is a differentiable scalar function of x, y, and z.

$$\nabla f = \mathbf{i}\frac{\partial f}{\partial x} + \mathbf{j}\frac{\partial f}{\partial y} + \mathbf{k}\frac{\partial f}{\partial z}$$

$$\nabla \times \nabla f = \mathbf{i}\left(\frac{\partial^2 f}{\partial y \partial z} - \frac{\partial^2 f}{\partial z \partial z}\right) + \mathbf{j}\left(\frac{\partial^2 f}{\partial z \partial x} - \frac{\partial^2 f}{\partial x \partial z}\right) + \mathbf{k}\left(\frac{\partial^2 f}{\partial x \partial y} - \frac{\partial^2 f}{\partial y \partial x}\right) = 0$$

This vanishes because each term vanishes by the Euler reciprocity relation.

Exercise 8.21. **a.** Find the h factors for cylindrical polar coordinates.

$$h_r = 1$$
$$h_\phi = \rho$$
$$h_z = 1$$

b. Find the expression for the gradient of a function of cylindrical polar coordinates, $f = f(\rho, \phi, z)$.

$$\nabla f = \mathbf{e}_\rho \frac{\partial f}{\partial \rho} + \mathbf{e}_\phi \frac{1}{r}\frac{\partial f}{\partial \phi} + \mathbf{k}\frac{\partial f}{\partial z}$$

c. Find the gradient of the function

$$f = e^{-(\rho^2+z^2)/a^2}\sin(\phi).$$

$$\begin{aligned}\nabla e^{-(\rho^2+z^2)/a^2}\sin(\phi) &= \mathbf{e}_\rho\left[\frac{-2\rho}{a^2}e^{-(\rho^2+z^2)/a^2}\sin(\phi)\right] \\ &\quad + \mathbf{e}_\phi \frac{1}{\rho} e^{-(\rho^2+z^2)/a^2}\cos(\phi) \\ &\quad + \mathbf{k}\left[-\frac{2z}{a^2}e^{-(\rho^2+z^2)/a^2}\sin(\phi)\right] \\ &= \mathbf{e}_\rho\left[\frac{-2\rho}{a^2}\sin(\phi)\right] + \mathbf{e}_\phi\frac{1}{r}\cos(\phi) \\ &\quad + \mathbf{k}\left[-\frac{2z}{a^2}\sin(\phi)\right]e^{-(\rho^2+z^2)/a^2}\end{aligned}$$

Exercise 8.22. Write the formula for the divergence of a vector function $\mathbf{F}$ expressed in terms of cylindrical polar coordinates. Note that $\mathbf{e}_z$ is the same as $\mathbf{k}$.

$$\nabla \cdot \mathbf{F} = \frac{1}{\rho}\left[\frac{\partial}{\partial \rho}(F_\rho \rho) + \frac{\partial}{\partial \phi}(F_\phi) + \frac{\partial}{\partial z}(F_z \rho)\right]$$

Exercise 8.23. Write the expression for the Laplacian of the function e^{-r^2}

$$\begin{aligned}\nabla^2 e^{-r^2} &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial e^{-r^2}}{\partial r}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2(-2r)\frac{1}{r^2}e^{-r^2}\right] \\ &= -\frac{2}{r^2}\frac{\partial}{\partial r}[re^{-r^2}] \\ &= -\frac{2}{r^2}(e^{-r^2} - 2r^2 e^{-r^2}) = \frac{2}{r^2}(2r^2-1)e^{-r^2} \\ &= 2\left(2 - \frac{1}{r^2}\right)e^{-r^2}\end{aligned}$$

PROBLEMS

1. A certain nonideal gas is described by the equation of state

$$\frac{PV_\mathrm{m}}{RT} = 1 + \frac{B_2}{V_\mathrm{m}}$$

where T is the temperature on the Kelvin scale, V_m is the molar volume, P is the pressure, and R is the gas constant. For this gas, the second virial coefficient B_2 is given as a function of T by

$$B_2 = [-1.00 \times 10^{-4} - (2.148 \times 10^{-6}) \times e^{(1956\ \mathrm{K})/T}]\mathrm{m}^3\ \mathrm{mol}^{-1},$$

Find $(\partial P/\partial V_\mathrm{m})_T$ and $(\partial P/\partial T)_{V_\mathrm{m}}$ and an expression for $\mathrm{d}P$.

$$P = \frac{RT}{V_\mathrm{m}} + \frac{RTB_2}{V_\mathrm{m}^2}$$

$$\left(\frac{\partial P}{\partial V_\mathrm{m}}\right)_T = -\frac{RT}{V_\mathrm{m}^2} - \frac{2RTB_2}{V_\mathrm{m}^3}$$

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_{V_\mathrm{m}} &= \frac{R}{V_\mathrm{m}} + \frac{RB_2}{V_\mathrm{m}^2} + \frac{RT}{V_\mathrm{m}^2}\left(\frac{dB_2}{\mathrm{d}T}\right) \\ &= \frac{R}{V_\mathrm{m}} + \frac{RB_2}{V_\mathrm{m}^2} + \text{need term here}\end{aligned}$$

$$\mathrm{d}P = \left[-\frac{RT}{V_\mathrm{m}^2} - \frac{2RTB_2}{V_\mathrm{m}^3} + \frac{RT}{V_\mathrm{m}^2}\left(\frac{dB_2}{\mathrm{d}T}\right)\right]\mathrm{d}T + \left(\frac{R}{V_\mathrm{m}} + \frac{RB_2}{V_\mathrm{m}^2}\right)\mathrm{d}V_\mathrm{m}$$

2. For a certain system, the thermodynamic energy U is given as a function of S, V, and n by

$$U = U(S, V, n) = Kn^{5/3}V^{-2/3}e^{2S/3nR},$$

where S is the entropy, V is the volume, n is the number of moles, K is a constant, and R is the ideal gas constant.

a. According to thermodynamic theory, $T = (\partial U/\partial S)_{V,n}$. Find an expression for $(\partial U/\partial S)_{V,n}$.

$$\begin{aligned}T &= \left(\frac{\partial U}{\partial S}\right)_{V,n} = Kn^{5/3}V^{-2/3}e^{2S/3nR}\frac{2}{3nR} \\ &= \frac{2U}{3nR}\end{aligned}$$

From this we can deduce

$$U = \frac{3}{2}nRT$$

which is the relation for a monatomic ideal gas with constant heat capacity

b. According to thermodynamic theory, the pressure $P = -(\partial U/\partial V)_{S,n}$. Find an expression for $(\partial U/\partial V)_{S,n}$.

$$\begin{aligned} P &= -\left(\frac{\partial U}{\partial V}\right)_{S,n} = \frac{2}{3}Kn^{5/3}V^{-5/3}e^{2S/3nR} \\ &= \frac{2U}{3V} = \frac{nRT}{V} \end{aligned}$$

which is the relation for an ideal gas.

c. According to thermodynamic theory, the chemical potential $\mu = -(\partial U/\partial n)_{S,V}$. Find an expression for $(\partial U/\partial n)_{S,V}$.

$$\begin{aligned} \mu &= \left(\frac{\partial U}{\partial n}\right)_{S,V} = \frac{5}{3}Kn^{2/3}V^{-5/3}e^{2S/3nR} \\ &\quad - Kn^{5/3}V^{-2/3}e^{2S/3nR}\left(\frac{2S}{3n^2R}\right) \\ &= \frac{5U}{3n} - \frac{2SU}{3n^2R} \\ &= \frac{5}{2}RT - \frac{TS}{n} = \frac{U}{n} + \frac{PV}{n} - \frac{TS}{n} = \frac{G}{n} \end{aligned}$$

where G is the Gibbs energy.

d. Find dU in terms of dS, dV, and dn.

$$\begin{aligned} dU &= \left(\frac{2U}{3nR}\right)dS - \left(\frac{2U}{3V}\right)dV \\ &\quad + \left(\frac{5U}{3n} - \frac{2SU}{3n^2R}\right)dn \\ &= T\,dS - P\,dV + \mu\,dn \end{aligned}$$

3. Find $(\partial f/\partial x)_y$, and $(\partial f/\partial y)_x$ for each of the following functions, where a, b, and c are constants.

a. $f = axy\ln(y)$

$$\left(\frac{\partial f}{\partial x}\right)_y = ay\ln(y)$$
$$\left(\frac{\partial f}{\partial y}\right)_x = ax\ln(y) + ax$$

b. $f = c\sin(x^2y)$

$$\left(\frac{\partial f}{\partial x}\right)_y = c\cos(x^2y)(2xy)$$
$$\left(\frac{\partial f}{\partial y}\right)_x = c\cos(x^2y)(x^2)$$

4. Find $(\partial f/\partial x)_y$, and $(\partial f/\partial y)_x$ for each of the following functions, where a, b, and c are constants.

a. $f = (x+y)/(c+x)$

$$\left(\frac{\partial f}{\partial x}\right)_y = \frac{y}{(c+x)} - \frac{x+y}{(c+x)^2}$$
$$\left(\frac{\partial f}{\partial y}\right)_x = \frac{x}{(c+x)}$$

b. $f = (ax+by)^{-2}$

$$\left(\frac{\partial f}{\partial x}\right)_y = \frac{-2a}{(ax+by)^3}$$
$$\left(\frac{\partial f}{\partial y}\right)_x = \frac{-2b}{(ax+by)^3}$$

5. Find $(\partial f/\partial x)_y$, and $(\partial f/\partial y)_x$ for each of the following functions, where a, b, and c are constants.

a. $f = a\cos^2(bxy)$

$$\left(\frac{\partial f}{\partial x}\right)_y = -2a\cos(bxy)a\sin(bxy)(by)$$
$$\left(\frac{\partial f}{\partial y}\right)_x = -2a\cos(bxy)a\sin(bxy)(bx)$$

b. $f = a\exp{-b(x^2+y^2)}$

$$\left(\frac{\partial f}{\partial x}\right)_y = a\exp(-b(x^2+y^2)(-2bx)$$
$$\left(\frac{\partial f}{\partial y}\right)_x = a\exp(-b(x^2+y^2)(-2by)$$

6. Find $(\partial^2 f/\partial x^2)_y, (\partial^2 f/\partial x\partial y), (\partial^2 f/\partial y\partial x)$, and $(\partial^2 f/\partial y^2)$, for each of the following functions, where a, b, and c are constants.

a. $f = (x+y)^{-2}$

$$\left(\frac{\partial f}{\partial x}\right)_y = -2\frac{1}{(x+y)^3}$$
$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = 6\frac{1}{(x+y)^4}$$
$$\left(\frac{\partial^2 f}{\partial y\partial x}\right) = 6\frac{1}{(x+y)^4}$$
$$\left(\frac{\partial f}{\partial y}\right)_x = -2\frac{1}{(x+y)^3}$$
$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = 6\frac{1}{(x+y)^4}$$
$$\left(\frac{\partial^2 f}{\partial x\partial y}\right) = 6\frac{1}{(x+y)^4}$$

b. $f = \cos(xy)$

$$\left(\frac{\partial f}{\partial x}\right)_y = -y\sin(xy)$$
$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = -y^2\cos(xy)$$
$$\left(\frac{\partial^2 f}{\partial y\partial x}\right) = -xy\cos(xy) - \sin(xy)$$
$$\left(\frac{\partial f}{\partial y}\right)_x = -x\sin(xy)$$
$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = -x^2\cos(xy)$$
$$\left(\frac{\partial^2 f}{\partial x\partial y}\right) = xy\cos(xy) - \sin(xy)$$

7. Find $(\partial^2 f/\partial x^2)_y, (\partial^2 f/\partial x\partial y), (\partial^2 f/\partial y\partial x)$, and $(\partial^2 f/\partial y^2)$, for each of the following functions, where a, b, and c are constants.

a. $f = e^{(ax^2+by^2)}$

$$\left(\frac{\partial f}{\partial x}\right)_y = e^{(ax^2+by^2)}(2ax)$$
$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = e^{(ax^2+by^2)}(2a) + e^{(ax^2+by^2)}(2ax)^2$$
$$\left(\frac{\partial^2 f}{\partial y\partial x}\right) = e^{(ax^2+by^2)}(2ax)(2by)$$
$$\left(\frac{\partial f}{\partial y}\right)_x = e^{(ax^2+by^2)}(2by)$$
$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = e^{(ax^2+by^2)}(2b) + e^{(ax^2+by^2)}(2by)^2$$
$$\left(\frac{\partial^2 f}{\partial x\partial y}\right) = e^{(ax^2+by^2)}(2ax)(2by)$$

b. $f = \ln(bx^2 + cy^2)$

$$\left(\frac{\partial f}{\partial x}\right)_y = \frac{1}{(bx^2+cy^2)}(2bx)$$
$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = \frac{1}{(bx^2+cy^2)}(2b) - \frac{1}{(bx^2+cy^2)^2}(2bx)^2$$
$$\left(\frac{\partial^2 f}{\partial y\partial x}\right) = -\frac{1}{(bx^2+cy^2)^2}(2bx)(2cy)$$
$$\left(\frac{\partial f}{\partial y}\right)_x = \frac{1}{(bx^2+cy^2)}(2cy)$$
$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = \frac{2}{(x^2+y^2)^3}(2x)^2 - \frac{2}{(x^2+y^2)^2}$$
$$= \frac{1}{(bx^2+cy^2)}(2c) - \frac{1}{(bx^2+cy^2)^2}(2cy)^2$$
$$\left(\frac{\partial^2 f}{\partial x\partial y}\right) = -\frac{1}{(bx^2+cy^2)^2}(2bx)(2cy)$$

8. Find $(\partial^2 f/\partial x^2)_y$, $(\partial^2 f/\partial x\partial y)$, $(\partial^2 f/\partial y\partial x)$, and $(\partial^2 f/\partial y^2)$, for each of the following functions, where a, b, and c are constants

a. $f = (x^2 + y^2)^{-1}$

$$\left(\frac{\partial f}{\partial x}\right)_y = -\frac{1}{(x^2+y^2)^2}(2x)$$
$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = \frac{2}{(x^2+y^2)^3}(2x)^2 - \frac{2}{(x^2+y^2)^2}$$
$$\left(\frac{\partial^2 f}{\partial y\partial x}\right) = \frac{2}{(x^2+y^2)^3}(2x)(2y)$$
$$\left(\frac{\partial f}{\partial y}\right)_x = -\frac{1}{(x^2+y^2)^2}(2y)$$
$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = \frac{2}{(x^2+y^2)^3}(2y)^2 - \frac{2}{(x^2+y^2)^2}$$
$$\left(\frac{\partial^2 f}{\partial x\partial y}\right) = \frac{2}{(x^2+y^2)^3}(2x)(2y)$$

b. $f = \sin(xy)$

$$\left(\frac{\partial f}{\partial x}\right)_y = y\cos(xy)$$
$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = -y^2\sin(xy)$$
$$\left(\frac{\partial^2 f}{\partial y\partial x}\right) = \cos(xy) - xy\sin(xy)$$
$$\left(\frac{\partial f}{\partial y}\right)_x = x\cos(xy)$$
$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = -x^2\sin(xy)$$
$$\left(\frac{\partial^2 f}{\partial x\partial y}\right) = \cos(xy) - xy\sin(xy)$$

9. Test each of the following differentials for exactness.

a. $\mathrm{d}u = \sec^2(xy)\mathrm{d}x + \tan(xy)\mathrm{d}y$

$$\frac{\partial}{\mathrm{d}y}[\sec^2(xy)] = 2\sec(xy)\sec(xy)\tan(xy)(x)$$
$$= 2x\sec^2(xy)\tan(xy)$$
$$\frac{\partial}{\mathrm{d}x}[\tan(xy)] = \sec^2(xy)(y)$$

The differential is not exact.

b. $\mathrm{d}u = y\sin(xy)\mathrm{d}x + x\sin(xy)\mathrm{d}y$

$$\frac{\partial}{\mathrm{d}y}[y\sin(xy)] = \sin(xy) + xy\cos(xy)$$
$$\frac{\partial}{\mathrm{d}x}[x\sin(xy)] = \sin(xy) + xy\cos(xy)$$

The differential is exact.

10. Test each of the following differentials for exactness.

a. $\mathrm{d}u = \frac{y}{1+x^2}\mathrm{d}x - \tan^{-1}(x)\mathrm{d}y$

$$\frac{\partial}{\mathrm{d}y}\left(\frac{y}{1+x^2}\right) = \frac{1}{1+x^2}$$
$$\frac{\partial}{\mathrm{d}x}\tan^{-1}(x) = \frac{1}{1+x^2}$$

The differential is exact.

b. $\mathrm{d}u = (x^2+2x+1)\mathrm{d}x + (y^2+5y+4)\mathrm{d}y$.

$$\frac{\partial}{\mathrm{d}y}(x^2+2x+1) = 0$$
$$\frac{\partial}{\mathrm{d}x}(y^2+5y+4) = 0$$

The differential is exact.

11. Test each of the following differentials for exactness.

a. $\mathrm{d}u = xy\,\mathrm{d}x + xy\,\mathrm{d}y$

$$\frac{\partial(xy)}{\mathrm{d}y} = x$$
$$\frac{\partial(xy)}{\mathrm{d}x} = y$$

The differential is not exact.

b. $\mathrm{d}u = ye^{axy}\,\mathrm{d}x + xe^{axy}\,\mathrm{d}y$.

$$\frac{\partial}{\mathrm{d}y}(ye^{axy}) = e^{axy} + axye^{axy}$$
$$\frac{\partial}{\mathrm{d}x}(xe^{axy}) = e^{axy} + axye^{axy}$$

The differential is exact.

12. If $u = RT\ln(aTVn)$ find $\mathrm{d}u$ in terms of $\mathrm{d}T$, $\mathrm{d}V$, and $\mathrm{d}n$, where R and a are constants.

$$\begin{aligned}\mathrm{d}u &= \left(\frac{\partial u}{\partial T}\right)_{V,n}\mathrm{d}T + \left(\frac{\partial u}{\partial V}\right)_{T,n}\mathrm{d}V + \left(\frac{\partial u}{\partial n}\right)_{T,V}\mathrm{d}n\\ &= \left[R\ln(aTVn) + \frac{RT}{aTVn}(aVn)\right]\mathrm{d}T\\ &\quad + \frac{RT}{aTVn}(aTn)\mathrm{d}V + \frac{RT}{aTVn}(aTV)\mathrm{d}n\end{aligned}$$

13. Complete the formula

$$\left(\frac{\partial S}{\partial V}\right)_{P,n} = \left(\frac{\partial S}{\partial V}\right)_{T,n} + ?$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial V}\right)_{T,n}\mathrm{d}V + \left(\frac{\partial S}{\partial T}\right)_{V,n}\mathrm{d}T$$

$$\begin{aligned}\left(\frac{\partial S}{\partial V}\right)_{P,n} &= \left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial V}\right)_{P,n}\\ &\quad + \left(\frac{\partial S}{\partial T}\right)_{V,n}\left(\frac{\partial T}{\partial V}\right)_{P,n}\\ &= \left(\frac{\partial S}{\partial V}\right)_{T,n} + \left(\frac{\partial S}{\partial T}\right)_{V,n}\left(\frac{\partial T}{\partial V}\right)_{P,n}\end{aligned}$$

14. Find the location of the minimum in the function

$$f = f(x,y) = x^2 - x - y + y^2$$

considering all real values of x and y. What is the value of the function at the minimum?

$$\left[\frac{\partial}{\mathrm{d}x}(x^2 - x - y + y^2)\right]_y = 2x - 1$$
$$\left[\frac{\partial}{\mathrm{d}y}(x^2 - x - y + y^2)\right]_x = -1 + 2y$$

$$2x - 1 = 0 \quad \text{if } x = 1/2$$
$$-1 + 2y = 0 \quad \text{if } y = 1/2$$

Test to see that this is a relative minimum:

$$\left[\frac{\partial^2}{\mathrm{d}x^2}(x^2 - x - y + y^2)\right]_y = 2$$
$$\left[\frac{\partial^2}{\mathrm{d}y^2}(x^2 - x - y + y^2)\right]_x = 2$$
$$\left[\frac{\partial^2}{\mathrm{d}x\mathrm{d}y}(x^2 - x - y + y^2)\right]_x = 0$$
$$D = 4$$

The test shows that we have a local minimum. The value of the function at the minimum is

$$f(1/2,1/2) = \frac{1}{4} - \frac{1}{2} - \frac{1}{2} + \frac{1}{4} = -\frac{1}{2}$$

15. Find the minimum in the function of the previous problem subject to the constraint $x + y = 2$. Do this by substitution and by the method of undetermined multipliers. On the constraint

$$\begin{aligned}y &= 2 - x\\ f &= x^2 - x - (2 - x) + (2 - x)^2\\ &= x^2 - 2 + 4 - 4x + x^2\\ &= 2x^2 - 4x + 2\end{aligned}$$

$$\begin{aligned}\frac{df}{dx} &= 4x - 4 = 0 \text{ at the minimum}\\ x &= 1 \text{ at the minimum}\\ y &= 2 - x = 1 \text{ at the minimum}\end{aligned}$$

Now use Lagrange's method. The constraint can be written

$$\begin{aligned}g(x,y) &= x + y - 2 = 0\\ u(x,y) &= x^2 - x - y + y^2 + \lambda(x + y - 2)\end{aligned}$$

The equations to be solved are

$$\begin{aligned}\left(\frac{\partial u}{\partial x}\right)_y &= 2x - 1 + \lambda = 0\\ \left(\frac{\partial u}{\partial y}\right)_x &= -1 + 2y + \lambda = 0\end{aligned}$$

Solve the second equation for λ:

$$\lambda = 1 - 2y$$

Substitute this into the first equation:

$$2x - 1 + 1 - 2y = 0$$

We know from the constraint that $y = 2 - x$ so that

$$\begin{aligned}2x - 1 + 1 - 2(2 - x) &= 0\\ 4x - 4 &= 0\\ x &= 1\\ y &= 1\end{aligned}$$

16. Find the location of the maximum in the function

$$f = f(x,y) = x^2 - 6x + 8y + y^2$$

considering the region $0 < x < 2$ and $0 < y < 2$. What is the value of the function at the maximum?

$$\begin{aligned}\frac{\partial f}{\partial x} &= 2x - 6\\ \frac{\partial f}{\partial y} &= 8 + 2y\end{aligned}$$

The relative extremum is at $x = 3$, $y = -4$, which is outside our region. The value of the function at this point is:

$$f(3, -4) = 9 - 18 - 32 + 16 = -25$$

Test to see if this is a maximum or a minimum:

$$\begin{aligned}\frac{\partial^2 f}{\partial x^2} &= 2\\ \frac{\partial^2 f}{\partial y^2} &= 2\\ \frac{\partial^2 f}{\partial y \partial y}&0\\ D &= (2)(2) - 0 = 4\end{aligned}$$

This is a local minimum. The maximum must be on the boundary of the region. On the boundary given by $x = 0$

$$\begin{aligned}f(0,y) &= 8y + y^2\\ \frac{df(0,y)}{dy} &= 8 + 2y\end{aligned}$$

This vanishes at $y = -4$, which is outside our region. Check the endpoints of this part of the boundary:

$$\begin{aligned}f(0,0) &= 0\\ f(0,2) &= 20\end{aligned}$$

On the boundary given by $y = 0$

$$\begin{aligned}f(x,0) &= x^2 - 6x\\ \frac{df}{dx} &= 2x - 6\end{aligned}$$

This vanishes at $x = 3$, which is outside our region. Check the endpoints of the part of the boundary

$$f(2,0) = 4 - 12 = -8$$

On the boundary given by $x = 2$

$$\begin{aligned}f(2,y) &= -8 + 8y + y^2\\ \frac{df(2,y)}{dy} &= 8 - 2y\end{aligned}$$

This vanishes at $y = 4$, which is outside our region. Test the endpoint of this part of the boundary that we have not already tested:

$$f(2,2) = 4 - 12 + 16 + 4 = 12$$

We have tested the four corners of our region and have found the maximum at (0,2). Check the final side of our region

$$\begin{aligned}f(x,2) &= x^2 - 6x + 20\\ \frac{df(x,2)}{dx} &= 2x - 6\end{aligned}$$

This vanishes at $x = 3$, which is outside our region. The maximum of our function is (0,2) and is equal to 20.

17. Find the maximum in the function of the previous problem subject to the constraint $x + y = 2$.

$$f(x,y) = x^2 - 6x + 8y + y^2$$

We replace y by $2 - x$:

$$\begin{aligned}f(x) &= x^2 - 6x - 8(2 - x) + (2 - x)^2\\ &= x^2 - 6x - 16 + 8x + 2 - 2x + x^2 = 2x^2 - 14\end{aligned}$$

$$\frac{df}{dx} = 4x$$

This vanishes at $x = 0$, corresponding to (0,2), which is on the boundary of our region. This constrained maximum must be at (0,2) or at (2,0). The value of the function at (0,2) is 20 and the value at (0,2) is 20. This is the same as the unconstrained maximum.

18. Neglecting the attractions of all other celestial bodies, the gravitational potential energy of the earth and the sun is given by

$$\mathcal{V} = -\frac{Gm_s m_e}{r},$$

where G is the universal gravitational constant, equal to 6.673×10^{-11} m^3 s^{-2} kg^{-1}, m_s is the mass of the sun, m_e is the mass of the earth, and r is the distance from the center of the sun to the center of the earth. Find an expression for the force on the earth due to the sun using spherical polar coordinates. Compare your result with that using Cartesian coordinates in the example in the chapter.

$$\begin{aligned}\mathbf{F} &= -\nabla\left(-\frac{Gm_s m_e}{r}\right) = -\mathbf{e_r}\frac{\partial}{\partial r}\left(-\frac{Gm_s m_e}{r}\right)\\ &= -\mathbf{e}_r\left(\frac{Gm_s m_e}{r^2}\right)\\ F &= \frac{Gm_s m_e}{r^2}\end{aligned}$$

This agrees with the result of the example.

19. Find an expression for the gradient of the function

$$\begin{aligned}f(x,y,z) &= \cos(xy)\sin(z)\\ \nabla f &= -iy\sin(xy)\sin(z) + jx\sin(xy)\sin(z)\\ &\quad + k\cos(xy)\cos(z)\end{aligned}$$

20. Find an expression for the divergence of the function

$$\begin{aligned}\mathbf{F} &= \mathbf{i}\sin^2(x) + \mathbf{j}\sin^2(y) + \mathbf{k}\sin^2(z)\\ \nabla\cdot F &= 2\sin(x)\cos(x) + 2\sin(y)\cos(y)\\ &\quad +2\sin(z)\cos(z)\end{aligned}$$

21. Find an expression for the Laplacian of the function

$$f = r^2\sin(\theta)\cos(\phi)$$

$$\begin{aligned}\nabla^2 f &= = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}r^2\sin(\theta)\cos(\phi)\right)\\ &\quad + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left[\sin(\theta)\frac{\partial}{\partial\theta}r^2\sin(\theta)\cos(\phi)\right]\\ &\quad + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}r^2\sin(\theta)\cos(\phi)\\ &= \frac{2\sin(\theta)\cos(\phi)}{r^2}\frac{\partial}{\partial r}(r^3)\\ &\quad + \frac{r^2\cos(\phi)}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}[\sin(\theta)\cos(\theta)]\\ &\quad - \frac{r^2}{r^2\sin^2(\theta)}\sin(\theta)\cos(\phi)\\ &= 6(\sin(\theta)\cos(\phi))\\ &\quad + \frac{\cos(\phi)}{\sin(\theta)}[\cos^2(\theta) - \sin^2(\theta)]\\ &\quad - \frac{1}{\sin^2(\theta)}\sin(\theta)\cos(\phi)\\ &= 6\sin(\theta)\cos(\phi) + \frac{\cos^2(\theta)\cos(\phi)}{\sin(\theta)}\\ &\quad - \sin(\theta)\cos(\phi) - \frac{\cos(\phi)}{\sin(\theta)}\\ &= \left[6\sin(\theta) + \frac{\cos^2(\theta)}{\sin(\theta)} - \frac{1}{\sin(\theta)}\right]\cos(\phi)\end{aligned}$$

Integral Calculus with Several Independent Variables

EXERCISES

Exercise 9.1. Show that the differential in the preceding example is exact.

The differential is

$$dF = (2x + 3y)dx + (3x + 4y)dy$$

We apply the test based on the Euler reciprocity theorem:

$$\frac{\partial}{\partial y}(2x + 3y) = 3$$

$$\frac{\partial}{\partial x}(3x + 4y) = 3$$

Exercise 9.2. a. Show that the following differential is exact:

$$dz = (ye^{xy})dx + (xe^{xy})dy$$

$$\frac{\partial}{\partial y}(ye^{xy}) = e^{xy} + xye^{xy}$$

$$\frac{\partial}{\partial x}(xe^{xy}) = e^{xy} + xye^{xy}$$

b. Calculate the line integral $\int_c dz$ on the line segment from (0,0) to (2,2). On this line segment, $y = x$ and $x = y$.

$$\int_c dz = \int_0^2 (xe^{x^2})dx + \int_0^2 (ye^{y^2})dy$$

$$= 2\int_0^2 (xe^{x^2})dx$$

We let $u = x^2$; $du = 2x\,dx$

$$2\int_0^2 (xe^{x^2})dx = \int_0^4 (e^u)du = e^4 - e^0 = e^4 - 1$$

c. Calculate the line integral $\int_c dz$ on the path going from (0,0) to (0,2) and then to (2,2) (a rectangular path).

On the first leg:

$$\int_c dz = \int_0^2 ((0)e^0)dx + 0 = 0$$

On the second leg

$$\int_c dz = 0 + \int_0^2 (2)e^{2y}\,dy$$

We let $w = 2y$; $dw = 2\,dy$

$$\int_0^2 (2)e^{2y}\,dy = \int_0^4 e^w\,dw = e^4 - 1$$

Exercise 9.3. Carry out the two line integral of $du = dx + x\,dy$ from (0,0) to (x_1, y_1):

a. On the rectangular path from (0,0) to $(0, y_1)$ and then to (x_1, y_1);

On the first leg

$$\int_c dz = 0 + \int_0^{y_1} 0\,dy = 0$$

On the second leg:

$$\int_c dz = \int_0^{x_1} dx + 0 = x_1$$

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The line integral is

$$\int_c (\mathrm{d}x + x\,\mathrm{d}y) = x_1$$

b. On the rectangular path from (0,0) to $(x_1,0)$ and then to (x_1, y_1).

On the first leg

$$\int_c \mathrm{d}z = \int_0^{x_1} \mathrm{d}x + 0 = x_1$$

On the second leg:

$$\int_c \mathrm{d}z = 0 + \int_0^{y_1} x_1\,\mathrm{d}y = x_1 y_1$$

The line integral is

$$\int_c (\mathrm{d}x + x\,\mathrm{d}y) = x_1 + x_1 y_1$$

The two line integrals do not agree, because the differential is not exact.

Exercise 9.4. Carry out the line integral of the previous example, $\mathrm{d}u = yz\,\mathrm{d}x + xz\,\mathrm{d}y + xy\,\mathrm{d}z$, on the path from (0,0,0) to (3,0,0) and then from (3,0,0) to (3,3,0) and then from (3,3,0) to (3,3,3).

On the first leg

$$y = 0, \quad z = 0$$

$$\int_c \mathrm{d}u = \int_0^3 (0)\mathrm{d}x + 0 + 0$$

On the second leg

$$x = 3, \quad z = 0$$

$$\int_c \mathrm{d}u = \int_0^3 (0)\mathrm{d}y + 0$$

On the third leg

$$x = 3, \quad y = 3$$

$$\int_c \mathrm{d}u = \int_0^3 (9)\mathrm{d}z = 27$$

The line integral on the specified path is

$$\int_c (yz\,\mathrm{d}x + xz\,\mathrm{d}y + xy\,\mathrm{d}z) = 0 + 0 + 27 = 27$$

The function with this exact differential is $u = xyz + C$ where C is a constant, and the line integral is equal to

$$z(3,3,3) - z(0,0,0) = 27 + C - 0 - C = 27$$

Exercise 9.5. A two-phase system contains both liquid and gaseous water, so its equilibrium pressure is determined by the temperature. Calculate the cyclic integral of $\mathrm{d}w_{\mathrm{rev}}$ for the following process: The volume of the system is changed from 10.00 l to 20.00 l at a constant temperature of 25.00 °C, at which the pressure is 24.756 torr. The system is then heated to a temperature of 100.0 °C at constant volume of 20.00 l. The system is then compressed to a volume of 10.00 l at a temperature of 100.0 °C, at which the pressure is 760.0 torr. The system is then cooled from 100.0 °C to a temperature of 25.00 °C at a constant volume of 10.00 l. Remember to use consistent units.

On the first leg

$$\begin{aligned}\int_C \mathrm{d}w_{\mathrm{rev}} &= -\int_C P\,\mathrm{d}V = -P\int_C \mathrm{d}V = -P\Delta V \\ &= -(23.756\ \mathrm{torr})\left(\frac{101325\ \mathrm{Pa}}{760\ \mathrm{torr}}\right) \\ &\quad \times (10.00\ \mathrm{l})\left(\frac{1\ \mathrm{m}^3}{1000\ \mathrm{l}}\right) = -31.76\ \mathrm{J}\end{aligned}$$

On the second leg

$$\int_C \mathrm{d}w_{\mathrm{rev}} = 0$$

On the third leg

$$\begin{aligned}&\int_C \mathrm{d}w_{\mathrm{rev}} = -\int_C P\,\mathrm{d}V = -P\Delta V \\ &-(760.0\ \mathrm{torr})\left(\frac{101325\ \mathrm{Pa}}{760.0\ \mathrm{torr}}\right)(-10.00\ \mathrm{l})\left(\frac{1\ \mathrm{m}^3}{1000\ \mathrm{l}}\right) \\ &= 1013\ \mathrm{J}\end{aligned}$$

On the fourth leg

$$\int_C \mathrm{d}w_{\mathrm{rev}} = 0$$

$$w_{\mathrm{rev}} = \oint \mathrm{d}w_{\mathrm{rev}} = -31.76\ \mathrm{J} + 1013\ \mathrm{J} = 981\ \mathrm{J}$$

The cyclic integral does not vanish because the differential is not exact.

Exercise 9.6. The thermodynamic energy of a monatomic ideal gas is temperature-independent, so that $\mathrm{d}U = 0$ in an isothermal process (one in which the temperature does not change). Evaluate w_{rev} and q_{rev} for the isothermal reversible expansion of 1.000 mol of a monatomic ideal gas from a volume of 15.50 l to a volume of 24.40 l at a constant temperature of 298.15 K.

$$\begin{aligned}\Delta U &= q + w\\ w_{\text{rev}} &= -\int_C P\,\mathrm{d}V = -nRT\int_{V_1}^{V_2}\frac{1}{V}\mathrm{d}V\\ &= -nRT\ln\left(\frac{V_2}{V_1}\right)\\ &= -(1.000\text{ mol})(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\\ &\quad\times(298.15\text{ K})\ln\left(\frac{24.40\text{ l}}{15.50\text{ l}}\right)\\ &= -1125\text{ J}\\ q_{rev} &= 1125\text{ J}\end{aligned}$$

The negative sign of w indicates that the system did work on its surroundings, and the positive sign of q indicates that heat was transferred to the system.

Exercise 9.7. Evaluate the double integral

$$\int_2^4\int_0^\pi x\sin^2(y)\mathrm{d}y\,\mathrm{d}x.$$

We integrate the dy integral and then the dx integral. We use the formula for the indefinite integral over y:

$$\begin{aligned}&\int_2^4\int_0^\pi x\sin^2(y)\mathrm{d}y\,\mathrm{d}x\\ &= \int_2^4 x\left[\frac{y}{2}-\frac{\sin(2y)}{4}\bigg|_0^\pi\right]\mathrm{d}x = \int_2^4 x\frac{\pi}{2}\mathrm{d}x\\ &= \frac{\pi}{2}\frac{x^2}{2}\bigg|_2^4 = \frac{\pi}{2}\left(\frac{16}{2}-\frac{4}{2}\right) = 3\pi\end{aligned}$$

Exercise 9.8. Find the volume of the solid object shown in Fig. 9.3. The top of the object corresponds to $f = 5.00 - x - y$, the bottom of the object is the x-y plane, the trapezoidal face is the x-f plane, and the large triangular face is the y-f plane. The small triangular face corresponds to $x = 3.00$.

$$V = \int_0^{3.00}\int_0^{5.00-x}(5.00-x-y)\mathrm{d}y\,\mathrm{d}x$$

The first integration is

$$\begin{aligned}&\int_0^{5.00-x}(5.00-x-y)\mathrm{d}y\\ &= (5.00y - xy - y^2/2)\Big|_0^{5.00-x}\\ &= 5.00(5.00-x) - 5.00x - \frac{25.00-10.00x+x^2}{2}\\ &= 12.50 - 5.00x + \frac{x^2}{2}\end{aligned}$$

$$\begin{aligned}V &= \int_0^{3.00}\left(12.50-5.00x+\frac{x^2}{2}\right)\mathrm{d}x = 12.50x\\ &\quad -\frac{5.00x^2}{2}+\frac{x^3}{6}\bigg|_0^{3.00}\\ &= 37.5 - 22.50 + \frac{27.00}{6} = 19.5\end{aligned}$$

Exercise 9.9. Find the value of the constant A so that the following integral equals unity.

$$A\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-x^2-y^2}\mathrm{d}y\,\mathrm{d}x.$$

The integral can be factored

$$\begin{aligned}&A\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-x^2-y^2}\,\mathrm{d}y\,\mathrm{d}x\\ &= A\int_{-\infty}^{\infty}e^{-x^2}\,\mathrm{d}x\int_{-\infty}^{\infty}e^{-y^2}\,\mathrm{d}y\end{aligned}$$

The integrals can be looked up in a table of definite integrals

$$\begin{aligned}&\int_{-\infty}^{\infty}e^{-x^2}\,\mathrm{d}x = 2\int_0^{\infty}e^{-x^2}\,\mathrm{d}x = \sqrt{\pi}\\ &A\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-x^2-y^2}\,\mathrm{d}y\,\mathrm{d}x = A\pi = 1\\ &A = \frac{1}{\pi}\end{aligned}$$

Exercise 9.10. Use a double integral to find the volume of a cone of height h and radius a at the base. If the cone is standing with its point upward and with its base centered at the origin, the equation giving the height of the surface of the cone as a function of ρ is

$$f = h\left(1-\frac{\rho}{a}\right).$$

$$\begin{aligned}V &= h\int_0^a\int_0^{2\pi}\left(1-\frac{\rho}{a}\right)\rho\,\mathrm{d}\phi\,\mathrm{d}\rho\\ &= 2\pi h\int_0^a\left(\rho-\frac{\rho^2}{a}\right)\rho\,\mathrm{d}\rho\\ &= 2\pi h\left(\frac{\rho^2}{2}-\frac{\rho^3}{3a}\right)\bigg|_0^a = 2\pi h\left(\frac{a^2}{2}-\frac{a^2}{3}\right) = \frac{\pi h a^2}{3}\end{aligned}$$

Exercise 9.11. Find the Jacobian for the transformation from Cartesian to cylindrical polar coordinates. Without resorting to a determinant, we find the expression for the element of volume in cylindrical polar coordinates:

$$\mathrm{d}V = \text{element of volume} = \rho\,\mathrm{d}\phi\,\mathrm{d}\rho\,\mathrm{d}z.$$

The Jacobian is
$$\frac{\partial(x,y,z)}{\partial(\rho,\phi,z)}=\rho$$

Exercise 9.12. Evaluate the triple integral in cylindrical polar coordinates:

$$I=\int_0^{3.00}\int_0^{4.00}\int_0^{2\pi} z\rho^3\cos^2(\phi)\mathrm{d}\phi\,\mathrm{d}\rho\,\mathrm{d}z$$

The integral can be factored:

$$I=\int_0^{2\pi}\cos^2(\phi)\mathrm{d}\phi\int_0^{4.00}\rho^3\,\mathrm{d}\rho\int_0^{3.00} z\,\mathrm{d}z$$

The ϕ integral can be looked up in a table of indefinite integrals:

$$\int_0^{2\pi}\cos^2(\phi)\mathrm{d}\phi=\left(\frac{\phi}{2}-\frac{\sin(2\phi)}{4}\right)\Big|_0^{2\pi}=\pi$$
$$\int_0^{4.00}\rho^3\mathrm{d}\rho=\frac{\rho^4}{4}\Big|_0^{4.00}=64.0$$
$$\int_0^{3.00} z\,\mathrm{d}z=\frac{z^2}{2}\Big|_0^{3}=\frac{9.00}{2}=4.50$$
$$I=4.50\times 64.0\times\pi=288\pi=905$$

PROBLEMS

1. Perform the line integral

$$\int_C \mathrm{d}u=\int_C (x^2y\,\mathrm{d}x+xy^2\,\mathrm{d}y),$$

a. on the line segment from (0,0) to (2,2). On this path, $x=y$, so

$$\int_C \mathrm{d}u\int_0^2 x^3\,\mathrm{d}x+\int_0^2 y^3\,\mathrm{d}y=\frac{x^4}{4}\Big|_0^2+\frac{y^4}{4}\Big|_0^2=\frac{16}{4}+\frac{16}{4}=8$$

b. on the path from (0,0) to (2,0) and then from (2,0) to (2,2). On the first leg of this path, $y=0$ and $\mathrm{d}y=0$, so both terms of the integral vanish on this leg. On the second leg, $x=2$ and $\mathrm{d}x=0$.

$$\int_C \mathrm{d}u=0+\int_0^2 2y^2\,\mathrm{d}y=2\,\frac{y^3}{3}\Big|_0^2=\frac{16}{3}$$

The two results do not agree, so the differential is not exact. Test for exactness:

$$\left[\frac{\partial}{\partial y}(x^2y)\right]_x=x^2$$
$$\left[\frac{\partial}{\partial x}(xy^2)\right]_y=y^2$$

The differential is not exact.

2. Perform the line integral

$$\int_C \mathrm{d}u=\int_C (y\,\mathrm{d}x+x\,\mathrm{d}y)$$

on the curve represented by

$$y=x^2$$

from (0,0) to (2,4).

$$\begin{aligned}\int_C \mathrm{d}u&=\int_C (x^2\,\mathrm{d}x+y^{1/2}\mathrm{d}y)\\&=\int_0^2 x^2\,\mathrm{d}x+\int_0^4 y^{1/2}\,\mathrm{d}y\\&=\left[\frac{x^3}{3}\right]_0^2+\left[\frac{y^{3/2}}{3/2}\right]_0^4\\&=\frac{8}{3}+\frac{8}{1.5}=8\end{aligned}$$

Note that $\mathrm{d}u$ is exact, so that

$$u=xy$$

the line integral is equal to

$$u(2,4)-u(0,0)=8$$

3. Perform the line integral

$$\int_C \mathrm{d}u=\int_C\left(\frac{1}{x}\mathrm{d}x+\frac{1}{y}\mathrm{d}y\right)$$

on the curve represented by

$$y=x$$

From (1,1) to (2,2).

$$\begin{aligned}\int_C \mathrm{d}u&=\int_1^2\frac{1}{x}\mathrm{d}x+\int_1^2\frac{1}{y}\mathrm{d}y\\&=[\ln(x)]_1^2+[\ln(y)]_1^2\\&=2[\ln(2)-\ln(1)]=2\ln(2)\end{aligned}$$

Note that $\mathrm{d}u$ is exact, so that

$$u=\ln(xy)$$

the line integral is equal to

$$u(2,2)-u(1,1)=\ln(2^2)-2\ln(2)=1.38629$$

4. Find the function whose differential is

$$\mathrm{d}f=\cos(x)\cos(y)\mathrm{d}x-\sin(x)\sin(y)\mathrm{d}y$$

and whose value at $x = 0$, $y = 0$ is 0. Test for exactness

$$\frac{\partial}{\partial y}[\cos(x)\cos(y)] = -\cos(x)\sin(y)$$
$$\frac{\partial}{\partial x}[-\sin(x)\sin(y)] = -\cos(x)\sin(y)$$

We integrate on a rectangular path from (0,0) to $(x_1,0)$ and then from $(x_1,0)$ to (x_1,y_1). On the first leg, $y = 0$ and $\mathrm{d}y = 0$. On the second leg, $x = x_1$ and $\mathrm{d}x = 0$. Since the differential is exact,

$$\begin{aligned}
&f(x_1,y_1) - f(0,0)\\
&= \int_C [\cos(x)\cos(y)\mathrm{d}x - \sin(x)\sin(y)\mathrm{d}y]\\
&= \int_0^{x_1} \cos(x)(1)\mathrm{d}x - \int_0^{y_1} \sin(x_1)\sin(y)\mathrm{d}y\\
&= \sin(x)|_0^{x_1} + \sin(x_1)\cos(y)|_0^{y_1}\\
&= \sin(x_1) + \sin(x_1)\cos(y_1) - \sin(x_1)\\
&= \sin(x_1)\cos(y_1)\\
&f(x,y) = \sin(x)\cos(y)
\end{aligned}$$

5. Find the function $f(x,y)$ whose differential is

$$\mathrm{d}f = (x+y)^{-1}\mathrm{d}x + (x+y)^{-1}\mathrm{d}y$$

and which has the value $f(1,1) = 0$. Do this by performing a line integral on a rectangular path from (1,1) to (x_1,y_1) where $x_1 > 0$ and $y_1 > 0$. Since the differential is exact,

$$\begin{aligned}
&f(x_1,y_1) - f(1,1)\\
&\quad = \int_C \left((x+y)^{-1}\mathrm{d}x + (x+y)^{-1}\mathrm{d}y\right)
\end{aligned}$$

We choose the path from (1,1) to $(1,x_1)$ and from $(1,x_1)$ to (x_1,y_1). On the first leg, $x = 1$ and $\mathrm{d}y = 0$. On the second leg, $x = x_1$ and $\mathrm{d}x = 0$

$$\begin{aligned}
&\int_C \left((x+y)^{-1}\mathrm{d}x + (x+y)^{-1}\mathrm{d}y\right)\\
&= \int_1^{x_1} \frac{1}{x+1}\mathrm{d}x + \int_1^{y_1} \frac{1}{x_1+y}\mathrm{d}y\\
&= \ln(x+1)|_1^{x_1} + \ln(x_1+y)|_1^{y_1}\\
&= \ln(x_1+1) - \ln(2) + \ln(x_1+y_1) - \ln(x_1+1)\\
&f(x_1,y_1) - f(1,1) = \ln(x_1+y_1) - \ln(2)
\end{aligned}$$

Since $f(1,1) = 0$ the function is

$$f(x,y) = \ln(x+y) - \ln(2)$$

where we drop the subscripts on x and y.

6. Find the function whose exact differential is

$$\begin{aligned}
\mathrm{d}f = {}& \cos(x)\sin(y)\sin(z)\mathrm{d}x\\
&+ \sin(x)\cos(y)\sin(z)\mathrm{d}y\\
&+ \sin(x)\sin(y)\cos(z)\mathrm{d}z
\end{aligned}$$

and whose value at (0,0,0) is 0. Since the differential is exact,

$$\begin{aligned}
&f(x_1,y_1,z_1) - f(0,0,0)\\
&\quad = \int_C [\cos(x)\sin(y)\sin(z)\mathrm{d}x\\
&\qquad + \sin(x)\cos(y)\sin(z)\mathrm{d}y\\
&\qquad + \sin(x)\sin(y)\cos(z)\mathrm{d}z]
\end{aligned}$$

where C represents any path from (0,0,0) to (x_1,y_1,z_1). We choose the rectangular path from (0,0,0) to $(x_1,0,0)$ and then to $(x_1,y_1,0)$ and then to (x_1,y_1,z_1). On the first leg, $y = 0, z = 0, \mathrm{d}y = 0, \mathrm{d}z = 0$. On the second leg, $x = x_1, z = 0, \mathrm{d}x = 0, \mathrm{d}z = 0$. On the third leg, $x = x_1, y = y_1, \mathrm{d}x = 0, \mathrm{d}y = 0$.

$$\begin{aligned}
\int_C \mathrm{d}f &= f(x_1,y_1,z_1) - f(0,0,0)\\
&= \int_0^{x_1} \cos(x)(0)\mathrm{d}x + \int_0^{x_1} \sin(x_1)(0)\mathrm{d}x\\
&\quad + \sin(x_1)\sin(y_1)\int_0^{z_1} \cos(z)\mathrm{d}z\\
&= \sin(x_1)\sin(y_1)\sin(z_1) - 0\\
f(x,y,z) &= \sin(x)\sin(y)\sin(z)
\end{aligned}$$

Find the area of the circle of radius a given by

$$\rho = a$$

by doing the double integral

$$\int_0^a \int_0^{2\pi} 1\rho\,\mathrm{d}\phi\,\mathrm{d}\rho.$$

$$A = \int_0^a \int_0^{2\pi} 1\rho\,\mathrm{d}\phi\,\mathrm{d}\rho = 2\pi \int_0^a \rho\,\mathrm{d}\rho$$
$$= 2\pi \left(\frac{\rho^2}{2}\right)\bigg|_0^a = \pi a^2$$

7. Find the moment of inertia of a uniform disk of radius 0.500m and a mass per unit area of 25.00 g m^2. The moment of inertia, is defined by

$$I = \iint m(\rho)\rho^2\,\mathrm{d}A = \int_0^R \int_0^{2\pi} m(\rho)\rho^2\rho\,\mathrm{d}\phi\,\mathrm{d}\rho$$

where $m(\rho)$ is the mass per unit area and R is the radius of the disk.

$$\begin{aligned}
I &= (25.00\ \mathrm{g\ m^{-2}})\left(\frac{1\ \mathrm{kg}}{1000\ \mathrm{g}}\right) \\
&\quad\times \int_0^{0.500\ \mathrm{m}}\int_0^{2\pi}\rho^2\rho\,\mathrm{d}\phi\,\mathrm{d}\rho \\
&= (0.02500\ \mathrm{kg\ m^{-2}})(2\pi)\int_0^{0.500\ \mathrm{m}}\rho^3\,\mathrm{d}\rho \\
&= (0.15708\ \mathrm{kg\ m^{-2}})\left(\frac{(0.500\ \mathrm{m})^4}{4}\right) \\
&= 0.002454\ \mathrm{kg\ m^2}
\end{aligned}$$

The mass of the disk is

$$\begin{aligned}
M &= \iint m(\rho)\mathrm{d}A = \int_0^R\int_0^{2\pi} m(\rho)\rho\,\mathrm{d}\phi\,\mathrm{d}\rho \\
&= 2\pi m(\rho)\int_0^R \rho\,\mathrm{d}\rho = 2\pi m(\rho)\frac{R^2}{2} \\
&= 2\pi(0.02500\ \mathrm{kg\ m^2})\left[\frac{(0.500\ \mathrm{m})^2}{2}\right] \\
&= 0.01963\ \mathrm{kg}
\end{aligned}$$

The standard formula from an elementary physics book is

$$\begin{aligned}
I &= \frac{1}{2}MR^2 = \frac{1}{2}(0.01963\ \mathrm{kg})(0.500\ \mathrm{m})^2 \\
&= 0.002454\ \mathrm{kg\ m^2}
\end{aligned}$$

8. A flywheel of radius R has a distribution of mass given by

$$m(\rho) = a\rho + b,$$

where ρ is the distance from the center, a and b are constants, and $m(\rho)$ is the mass per unit area as a function of ρ. The flywheel has a circular hole in the center with radius r. Find an expression for the moment of inertia, defined by

$$I = \iint m(\rho)\rho^2\,\mathrm{d}A = \int_0^R\int_0^{2\pi} m(\rho)\rho^2\rho\,\mathrm{d}\phi\,\mathrm{d}\rho,$$

$$\begin{aligned}
I &= \int_r^R\int_0^{2\pi}(a\rho+b)\rho^2\rho\,\mathrm{d}\phi\,\mathrm{d}\rho \\
&= \int_r^R\int_0^{2\pi}(a\rho^4+b\rho^3)\mathrm{d}\phi\,\mathrm{d}\rho \\
&= 2\pi\int_r^R(a\rho^4+b\rho^3)\mathrm{d}\rho = 2\pi\left[\frac{a\rho^5}{4}+\frac{b\rho^4}{3}\right]\Bigg|_r^R \\
&= 2\pi\left[\frac{aR^5}{4}+\frac{bR^4}{3}\right] - 2\pi\left[\frac{ar^5}{4}+\frac{br^4}{3}\right]
\end{aligned}$$

9. Find an expression for the moment of inertia of a hollow sphere of radius a, a thickness Δa, and a uniform mass per unit volume of m. Evaluate your expression if $a = 0.500$ m, $\Delta a = 0.112$ mm, $m = 3515\ \mathrm{kg\ m^{-3}}$.

$$\begin{aligned}
I &= \int_a^{a+\Delta a}\int_0^{\pi}\int_0^{2\pi} mr^2r^2\sin(\theta)\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d} \\
r &= 2\pi\int_a^{a+\Delta a}\int_0^{\pi} mr^2r^2\sin(\theta)\mathrm{d}\theta\,\mathrm{d}r \\
&= (2)2\pi\int_a^{a+\Delta a} mr^4\,\mathrm{d}r \\
&= 4\pi m\left[\frac{(a+\Delta a)^5}{5}-\frac{a^5}{5}\right]
\end{aligned}$$

Expanding the polynomial

$$\begin{aligned}
(a+\Delta a)^5 &= a^5 + 5a^4\Delta a + 10a^3\Delta a^2 + 10a^2\Delta a^3 \\
&\quad + 5a\Delta a^4 + \Delta a^5
\end{aligned}$$

If Δa is small, so that we can ignore Δa^2 compare with Δa,

$$\begin{aligned}
(a+\Delta a)^5 - a^5 &\approx 5a^4\Delta a \\
I &\approx 4\pi m a^4\Delta a
\end{aligned}$$

We apply this approximation

$$\begin{aligned}
I &\approx 4\pi(3515\ \mathrm{kg\ m^{-3}})(0.500\ \mathrm{m})^4(0.112\ \mathrm{mm}) \\
&\quad\times\left(\frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}\right) = 0.309\ \mathrm{kg\ m^2}
\end{aligned}$$

10. Derive the formula for the volume of a sphere by integrating over the interior of a sphere of radius a with a surface given by $r = a$

$$\begin{aligned}
V &= \int_0^a\int_0^{\pi}\int_0^{2\pi} r^2\sin(\theta)\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}r \\
&= 2\pi\int_0^a\int_0^{\pi} r^2\sin(\theta)\mathrm{d}\theta\,\mathrm{d}r \\
&= -2\pi\int_0^a r^2\,\mathrm{d}r[\cos(\pi)-\cos(0)] \\
&= 4\pi\int_0^a r^2\,\mathrm{d}r = 4\pi\left(\frac{a^3}{3}\right) = \frac{4}{3}\pi a^3
\end{aligned}$$

11. Derive the formula for the volume of a right circular cylinder of radius a and height h.

$$\begin{aligned}
V &= \int_0^h\int_0^a\int_0^{2\pi}\rho\,\mathrm{d}\phi\,\mathrm{d}\rho\,\mathrm{d}z \\
&= 2\pi\int_0^h\int_0^a\rho\,\mathrm{d}\rho\,\mathrm{d}z \\
&= 2\pi\int_0^h\int_0^a\rho\,\mathrm{d}\rho\,\mathrm{d}z \\
&= 2\pi\int_0^h\mathrm{d}z\left(\frac{a^2}{2}\right) = \pi a^2h
\end{aligned}$$

12. Find the volume of a cup obtained by rotating the parabola

$$z = 4.00\rho^2$$

around the z axis and cutting off the top of the paraboloid of revolution at $z = 4.00$.

$$V = \int_0^{1.00} \int_{4.00\rho^2}^{4.00} \int_0^{2\pi} \rho \, d\phi \, dz \, d\rho$$

Since the limits of the z integration depend on ρ, the z integration must be done before the ρ integration. Note that $\rho = 1.00$ when $z = 1.00$ on the parabola.

$$\begin{aligned} V &= 2\pi \int_0^{1.00} \int_{4.00\rho^2}^{4.00} \rho \, dz \, d\rho \\ &= 2\pi \int_0^{1.00} \rho \, d\rho (4.00 - 4.00\rho^2) \\ &= 8.00\pi \int_0^{1.00} \rho \, d\rho - 8.00\pi \int_0^{1.00} \rho^3 \, d\rho \\ &= 8.00\pi \left(\frac{1.00}{2}\right) - 8.00\pi \left(\frac{1.00}{4}\right) \\ &= 2.00\pi = 6.28 \end{aligned}$$

13. Find the volume of a right circular cylinder of radius $a = 4.00$ with a paraboloid of revolution scooped out of the top of it such that the top surface is given by

$$z = 10.00 + 1.00\rho^2$$

and the bottom surface is given by $z = 0.00$.

$$V = \int_0^{2.00} \int_{0.00}^{10.00+1.00\rho^2} \int_0^{2\pi} \rho \, d\phi \, dz \, d\rho$$

The limit on ρ is obtained from the fact that $\rho = 2.00$ when the parabola intersects with the cylinder.

$$\begin{aligned} V &= 2\pi \int_0^{2.00} \int_{0.00}^{10.00+1.00\rho^2} \rho \, dz \, d\rho \\ &= 2\pi \int_0^{2.00} \rho \, d\rho [10.00 + 1.00\rho^2] \\ &= 20.00\pi \left(\frac{4.00}{2}\right) + 2.00\pi \left(\frac{8}{3}\right) \\ &= 40.00\pi + \frac{16.00\pi}{3} = 142.4 \end{aligned}$$

14. Find the volume of a solid with vertical walls such that its base is a square in the $x - y$ plane defined by $0 \leqslant x \leqslant 2.00$ and $0 \leqslant x \leqslant 2.00$ and its top is defined by the plane $z = 20.00 + x + y$.

$$\begin{aligned} V &= \int_0^{2.00} \int_0^{2.00} \int_0^{20.00+x+y} dz \, dx \, dy \\ &= \int_0^{2.00} \int_0^{2.00} (20.00 + x + y) dx \, dy \end{aligned}$$

The z integration must be done first, since its limits depend on x and y. We do the x integration next, followed by the y integration:

$$\begin{aligned} V &= \int_0^{2.00} \left((20.00)(2.00) + \frac{(2.00)^2}{2} + 2.00y \right) dy \\ &= (42.00)(2.00)) + 2.00 \left(\frac{4.00}{2}\right) = 88.00 \end{aligned}$$

15. Find the volume of a solid produced by scooping out the interior of a circular cylinder of radius 10.00 cm and height 12.00 cm so that the inner surface conforms to $z = 2.00 \text{ cm} + (0.01000 \text{ cm}^{-2})\rho^3$.

$$\begin{aligned} V &= \int_0^{10.00 \text{ cm}} \int_0^{2\pi} \\ &\quad \times \left[2.00 \text{ cm} + (0.01000 \text{ cm}^{-2})\rho^3 \right] \rho \, d\rho \, d\phi \\ &= \int_0^{2\pi} d\phi \\ &\quad \times \left[\frac{2.00 \text{ cm}}{2} \rho^2 + \left(\frac{0.01000 \text{ cm}^{-2}}{5} \right) \rho^5 \right]_{0.00}^{10.00 \text{ cm}} \\ &= (2\pi) \Big[100.0 \text{ cm}^3 + (0.00200 \text{ cm}^{-2}) \\ &\qquad \times (1.00 \times 10^5 \text{ cm}^5) \Big] \\ &= 1885 \text{ cm}^3 \end{aligned}$$

16. Find the moment of inertia of a ring with radius 10.00 cm, width 0.25 cm and a mass of 0.100 kg

$$\begin{aligned} I &= \iint m(\rho)\rho^2 \, dA \\ &= \int_{9.75 \text{ cm}}^{10.00 \text{ cm}} \int_0^{2\pi} m(\rho)\rho^2 \rho \, d\phi \, d\rho \\ &= 2\pi \int_{9.75 \text{ cm}}^{10.00 \text{ cm}} m(\rho)\rho^3 \, d\rho \\ &\approx 2\pi m(\rho) \int_{9.75 \text{ cm}}^{10.00 \text{ cm}} \rho^3 \, d\rho \\ &= 2\pi m(\rho) \left[\frac{\rho^4}{4} \right]_{9.75 \text{ cm}}^{10.00 \text{ cm}} \\ &= \frac{2\pi m(\rho)}{4} \left[(10.00 \text{ cm})^4 - (9.75 \text{ cm})^4 \right] \\ &= \frac{\pi m(\rho)}{2} (983.12 \text{ cm}^4) = (1512.9 \text{ cm}^4) m(\rho) \end{aligned}$$

where have factored $m(\rho)$ out of the integral since the width is small. We now need to find a value for $m(\rho)$. The mass of the ring is given by

$$M = 2\pi \int_{9.75 \text{ cm}}^{10.00 \text{ cm}} m(\rho)\rho \, d\rho$$

Since 0.25 cm is quite small compared with 10.00 cm, we factor $m(\rho)$ out of the integral

$$\begin{aligned} M &= 2\pi m(\rho)\int_{9.75\text{ cm}}^{10.00\text{ cm}} \rho^2\, \mathrm{d}\rho \\ &= \frac{2\pi m(\rho)}{2}\left[(10.00\text{ cm})^2 - (9.75\text{ cm})^2\right] \\ 0.100\text{ kg} &= (\pi m(\rho))\left[100.0\text{ cm}^2 - 95.0625\text{ cm}^2\right] \\ &= 15.512\text{ cm}^2 m(\rho) \\ m(\rho) &= \frac{0.100\text{ kg}}{15.512\text{ cm}^2} \\ &= 6.4468\times 10^{-3}\text{ kg cm}^{-2} \\ I &= (1512.9\text{ cm}^4)m(\rho) \\ &= (1512.9\text{ cm}^4)\left(6.4468\times 10^{-3}\text{ kg cm}^{-2}\right) \\ &= 9.753\text{ kg cm}^2\left(\frac{1\text{ m}}{100\text{ cm}}\right)^2 \\ &= 9.753\times 10^{-4}\text{ kg m}^2 \end{aligned}$$

From an elementary physics textbook, the formula for a thin ring is

$$\begin{aligned} I &= MR^2 = (0.100\text{ kg})(0.0100\text{ m})^2 \\ &= 1.00\times 10^{-5}\text{ kg m}^2 \end{aligned}$$

17. Find the moment of inertia of a flat rectangular plate with dimensions 0.500 m by 0.400 m around an axis through the center of the plate and perpendicular to it. Assume that the plate has a mass $M = 2.000$ kg and that the mass is uniformly distributed.

$$I = \int_{-0.250\text{ m}}^{0.250\text{ m}}\int_{-0.200\text{ m}}^{0.200\text{ m}} m(x^2+y^2)\mathrm{d}x\,\mathrm{d}y$$

where we let m be the mass per unit area.

$$m = \frac{2.000\text{ kg}}{0.200\text{ m}^2} = 10.00\text{ kg m}^2$$

$$\begin{aligned} I &= \int_{-0.250\text{ m}}^{0.250\text{ m}}\int_{-0.200\text{ m}}^{0.200\text{ m}} mx^2\,\mathrm{d}x\,\mathrm{d}y + I \\ &= \int_{-0.250\text{ m}}^{0.250\text{ m}}\int_{-0.200\text{ m}}^{0.200\text{ m}} my^2\,\mathrm{d}x\,\mathrm{d}y \\ &= (0.500\text{ m})\int_{-0.200\text{ m}}^{0.200\text{ m}} mx^2\,\mathrm{d}x \\ &\quad +(0.400\text{ m})\int_{-0.250\text{ m}}^{0.250\text{ m}} my^2\,\mathrm{d}y \\ &= (0.500\text{ m})\frac{1}{3}m[x^3]_{-0.200\text{ m}}^{0.200\text{ m}} \\ &\quad +(0.400\text{ m})\frac{1}{3}m\left[y^3\right]_{-0.250\text{ m}}^{0.250\text{ m}} \\ &= (0.500\text{ m})\frac{2}{3}m(0.200\text{ m})^3 \\ &\quad +(0.400\text{ m})\frac{2}{3}m(0.250\text{ m})^3 \\ &= (0.500\text{ m})\frac{2}{3}(10.00\text{ kg m}^{-2})(0.00800\text{ m}^3) \\ &\quad +(0.400\text{ m})\frac{2}{3}(10.00\text{ kg m}^{-2})(0.015625\text{ m}^3) \\ &= 0.02667\text{ kg m}^2 + 0.04167\text{ kg m}^2 \\ &= 0.06833\text{ kg m}^2 \end{aligned}$$

From an elementary physics textbook

$$I = \frac{1}{12}M(a^2+b^2)$$

where a and b are the dimensions of the plate. From this formula

$$\begin{aligned} I &= \left(\frac{1}{12}\right)(2.000\text{ kg})\left[(0.400\text{ m})^2 + (0.500\text{ m})^2\right] \\ &= 0.06833\text{ kg m}^2 \end{aligned}$$

18. Find the volume of a circular cylinder of radius 0.1000 m centered on the z axis, with a bottom surface given by the $x-y$ plane and a top surface given by $z = 0.1000\text{ m} + 0.500y$.

$$\begin{aligned} V &= \int_0^{0.100\text{ m}}\int_0^{2\pi} z\rho\,\mathrm{d}\phi\,\mathrm{d}\rho \\ &= \int_0^{0.100\text{ m}}\int_0^{2\pi} (0.1000\text{ m} + 0.500y)\rho\,\mathrm{d}\phi\,\mathrm{d}\rho \\ &= \int_0^{0.100\text{ m}}\int_0^{2\pi} \big[0.1000\text{ m} \\ &\qquad + 0.500\text{ m}\rho\sin(\phi)\big]\rho\,\mathrm{d}\phi\,\mathrm{d}\rho \end{aligned}$$

$$= \int_0^{0.100\ \mathrm{m}} \int_0^{2\pi} [0.1000\ \mathrm{m}]\rho\, \mathrm{d}\phi\, \mathrm{d}\rho$$
$$+ \int_0^{0.100\ \mathrm{m}} \int_0^{2\pi} [0.500\ \mathrm{m} \sin(\phi)]\rho\, \mathrm{d}\phi\, \mathrm{d}\rho$$
$$= 2\pi[0.1000\ \mathrm{m}] \int_0^{0.100\ \mathrm{m}} \rho \mathrm{d}\rho$$
$$+(0.500\ \mathrm{m}) \int_0^{0.100\ \mathrm{m}} \int_0^{2\pi} [\sin(\phi)]\rho\, \mathrm{d}\phi\, \mathrm{d}\rho$$
$$= 2\pi[0.1000\ \mathrm{m}] \left[\frac{(0.100\ \mathrm{m})^2}{2}\right]$$
$$+(0.500\ \mathrm{m}) \int_0^{0.100\ \mathrm{m}} \rho\, \mathrm{d}\rho [-\cos(\phi)]_0^{2\pi}$$
$$= \pi(0.00100\ \mathrm{m}^3) + 0 = 0.003142\ \mathrm{m}^3$$

Note that this is the same as the volume of a cylinder with height 0.100 m.

Chapter 10

Mathematical Series

EXERCISES

Exercise 10.1. Show that in the series of Eq. (10.4) any term of the series is equal to the sum of all the terms following it. (Hint: Factor a factor out of all of the following terms so that they will equal this factor times the original series, whose value is now known.)

Let the given term be denoted by

$$\text{term} = \frac{1}{2^n}$$

The following terms are

$$\begin{aligned}&\frac{1}{2^{n+1}} + \frac{1}{2^{n+2}} + \frac{1}{2^{n+3}} + \frac{1}{2^{n+4}} + \cdots\\ &= \frac{1}{2^{n+1}}\left(1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \cdots + \frac{1}{2^n} + \cdots\right)\\ &= \frac{2}{2^{n+1}} = \frac{1}{2^n}\end{aligned}$$

Exercise 10.2. Consider the series

$$s = 1 + \frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \cdots + \frac{1}{n^2} + \cdots$$

which is known to be convergent and to equal $\pi^2 6/ = 1.64993\cdots$. Using Eq. (10.5) as an approximation, determine which partial sum approximates the series to

a. 1%
1% of 1.64993 is equal to 0.016449. The $n = 8$ term is equal to 0.015625, so we need the partial sum S_8, which is equal to $1.2574\cdots$. The series is slowly convergent and S_8 is equal to 1.5274, so this approximation does not work very well.

b. 0.001%.
0.001% of 1.64993 is equal to 0.00016449. The $n = 79$ term is equal to 0.0001602, so we need the partial sum S_{79}. However, this partial sum is equal to 1.6324, so again this approximation does not work very well.

Exercise 10.3. Find the value of the infinite series

$$\sum_{n=0}^{\infty}[\ln(2)]^n$$

Determine how well this series is approximated by S_2, S_5, and S_{10}.

This is a geometric series, so the sum is

$$s = \frac{1}{1-\ln(2)} = 3.25889\cdots$$

The partial sums are

$$\begin{aligned}S_2 &= 1 + \ln(2) = 1.693\cdots\\ S_5 &= 1 + \ln(2) + \ln(2)^2 + \ln(2)^3 + \ln(2)^4\\ &= 2.73746\cdots\\ S_{10} &= 3.175461\\ S_{20} &= 3.256755\cdots\end{aligned}$$

Exercise 10.4. Evaluate the first 20 partial sums of the harmonic series.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00034-3

Here are the first 20 partial sums, obtained with Excel:

1
1.5
1.833333333
2.083333333
2.283333333
2.45
2.592857143
2.717857143
2.828968254
2.928968254
3.019877345
3.103210678
3.180133755
3.251562327
3.318228993
3.380728993
3.439552523
3.495108078
3.547739657
3.597739657

Exercise 10.5. Show that the geometric series converges if $r^2 \prec 1$.

If r is positive, we apply the ratio test:

$$\lim_{n\to\infty} \frac{a_{n+1}}{a_n} = r$$

If $r^2 \prec 1$ and if r is positive, then $r \prec 1$, so the series converges. If r is negative, apply the alternating series test. Each term is smaller than the previous term and approaches zero as you go further into the series, so the series converges.

Exercise 10.6. Test the following series for convergence.

$$\sum_{n=1}^{\infty} \frac{1}{n^2}$$

Apply the ratio test:

$$r = \lim_{n\to\infty} \frac{1/(n+1)^2}{1/n^2} = \lim_{n\to\infty} \left(\frac{n^2}{(n+1)^2} \right) = 1$$

The ratio test fails. We apply the integral text:

$$\int_1^{\infty} \frac{1}{x^2} \mathrm{d}x = - \left(\frac{1}{x} \right) \Big|_1^{\infty} = 1$$

The integral converges, so the series converges.

Exercise 10.7. Show that the Maclaurin series for e^x is

$$e^x = 1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \frac{1}{4!}x^4 + \cdots$$

Every derivative of e^x is equal to e^x

$$a_n = \frac{1}{n!} \left(\frac{\mathrm{d}^n f}{\mathrm{d}x^n} \right)_{x=0} = \frac{1}{n!}$$

Exercise 10.8. Find the Maclaurin series for $\ln(1 + x)$. You can save some work by using the result of the previous example.

The series is

$$\ln(1 + x) = a_0 + a_1 x + a_2 x^2 + \cdots$$

$$a_0 = \ln(1) = 0$$

$$\left. \frac{\mathrm{d}f}{\mathrm{d}x} \right|_{x=0} = \left. \frac{1}{1+x} \right|_{x=0} = 1$$

The second derivative is

$$\left. \frac{\mathrm{d}^2 f}{\mathrm{d}x^2} \right|_{x=0} = (-1) \left. \frac{1}{(1+x)^2} \right|_{x=0} = -1$$

The derivatives follow a pattern:

$$\left(\frac{\mathrm{d}^n f}{\mathrm{d}x^n} \right)_{x=1} = (-1)^{n-1} \left. \frac{(n-1)!}{(1+x)^n} \right|_{x=0} = (-1)^{n-1} (n-1)!$$

$$\frac{1}{n!} \left(\frac{\mathrm{d}^n f}{\mathrm{d}x^n} \right)_{x=1} = \frac{(-1)^{n-1}}{n}$$

The series is

$$\ln(1+x) = x - \left(\frac{1}{2}\right) x^2 + \left(\frac{1}{3}\right) x^3 - \left(\frac{1}{4}\right) x^4 + \left(\frac{1}{5}\right) x^5 + \cdots$$

Exercise 10.9. Find the Taylor series for $\ln(x)$, expanding about $x = 2$, and show that the radius of convergence for this series is equal to 2, so that the series can represent the function in the region $0 \prec x \leqslant 4$.

The first term is determined by letting $x = 2$ in which case all of the terms except for a_0 vanish:

$$a_0 = \ln(2)$$

The first derivative of $\ln(x)$ is $1/x$, which equals $1/2$ at $x = 2$. The second derivative is $-1/x^2$, which equals $-1/4$ at $x = 2$. The third derivative is $2!/x^3$, which equals $1/4$ at $x = 1$. The derivatives follow a regular pattern,

$$\left(\frac{\mathrm{d}^n f}{\mathrm{d}x^n} \right)_{x=2} = (-1)^{n-1} \left. \frac{(n-1)!}{x^n} \right|_{x=2} = (-1)^{n-1} \frac{(n-1)!}{2^n}$$

so that

$$\frac{1}{n!} \left(\frac{\mathrm{d}^n f}{\mathrm{d}x^n} \right)_{x=1} = \frac{(-1)^{n-1}}{n 2^n}$$

and

$$\ln(x) = \ln(2) + (x-2) - \frac{1}{8}(x-2)^2 + \frac{1}{24}(x-2)^3 - \frac{1}{64}(x-2)^4 + \cdots$$

The function is not analytic at $x = 0$, so the series is not valid at $x = 0$. For positive values of x the series is alternating, so we apply the alternating series test:

$$t_n = a_n(x-2)^n = \frac{(x-2)^n(-1)^{n-1}}{n2^n}$$
$$\lim_{n\to\infty}|t_n| = \begin{cases} 0 & \text{if}|x-2| \prec 2 \text{ or } 0 \prec x \leqslant 4 \\ \infty & \text{if}|x-2| > 2 \text{ or } x > 4. \end{cases}$$

Exercise 10.10. Find the series for $1/(1-x)$, expanding about $x = 0$. What is the interval of convergence?

$$\frac{1}{1+x} = a_0 + a_1 x + a_2 x^2 + \cdots$$

$$a_0 = 1$$
$$a_1 = \frac{d}{dx}\left(\frac{1}{1+x}\right)\bigg|_{x=0} = -\frac{1}{(1+x)^2}\bigg|_{x=0} = -1$$
$$a_2 = \frac{1}{2!}\frac{d}{dx}\left(\frac{1}{(1+x)^2}\right)\bigg|_{x=0} = \frac{2}{2!} - \frac{1}{(1+x)^3}\bigg|_{x=0} = 1$$

The pattern continues:

$$a_n = (-1)^n$$
$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + x^4 - x^5 + \cdots$$

Since the function is not analytic at $x = -1$, the interval of convergence is $-1 \prec x \prec 1$

Exercise 10.11. Find the relationship between the coefficients A_3 and B_3.

We begin with the virial equation of state

$$P = \frac{RT}{V_m} + \frac{RTB_2}{V_m^2} + \frac{RTB_3}{V_m^3} + \cdots$$

We write the pressure virial equation of state:

$$P = \frac{RT}{V_m} + \frac{A_2 P}{V_m} + \frac{A_3 P^2}{V_m} + \cdots$$

We replace P and P^2 in this equation with the expression from the virial equation of state:

$$P = \frac{RT}{V_m} + \frac{A_2}{V_m}\left(\frac{RT}{V_m} + \frac{RTB_2}{V_m^2} + \frac{RTB_3}{V_m^3} + \cdots\right) + \frac{A_3}{V_m}\left(\frac{RT}{V_m} + \frac{RTB_2}{V_m^2} + \frac{RTB_3}{V_m^3} + \cdots\right)^2 + \cdots$$

We use the expression for the square of a power series from Eq. (5) of Appendix C, part 2:

$$\left(\frac{RT}{V_m} + \frac{RTB_2}{V_m^2} + \frac{RTB_3}{V_m^3} + \cdots\right)^2 = \left(\frac{RT}{V_m}\right)^2 + 2\left(\frac{RT}{V_m}\right)\left(\frac{RTB_2}{V_m^2}\right) + O\left(\frac{1}{V_m}\right)^4 = \left(\frac{RT}{V_m}\right)^2 + 2\left(\frac{R^2T^2B_2}{V_m^3}\right) + O\left(\frac{1}{V_m}\right)^4$$

$$P = \frac{RT}{V_m} + \frac{A_2}{V_m}\left(\frac{RT}{V_m} + \frac{RTB_2}{V_m^2} + \frac{RTB_3}{V_m^3} + \cdots\right) + \frac{A_3}{V_m}\left(\left(\frac{RT}{V_m}\right)^2 + 2\left(\frac{R^2T^2B_2}{V_m^3}\right) + O\left(\frac{1}{V_m}\right)^4\right) + \cdots = \frac{RT}{V_m} + \frac{RTA_2}{V_m^2} + \frac{RTA_2B_2}{V_m^3} + \frac{A_3}{V_m}\left(\frac{RT}{V_m}\right)^2 = \frac{RT}{V_m} + \frac{RTB_2}{V_m^2} + \frac{RTB_2^2}{V_m^3} + \frac{A_3R^2T^2}{V_m^3}$$

where we have replaced A_2 by B_2. We now equation coefficients of equal powers of $(1/V_m)^2$ in the two series for P:

$$RTB_3 = RTB_2^2 + A_3R^2T^2$$
$$A_3 = B_3 - RTB_2^2$$

Exercise 10.12. Determine how large X_2 can be before the truncation of Eq. (10.28) that was used in Eq. (10.16) is inaccurate by more than 1%.

$$-\ln(X_1) = -\ln(1-X_2) = X_2 - \frac{1}{2}X_2^2 + \cdots$$

If the second term is smaller than 1% of the first term (which was the only one used in the approximation) the approximation should be adequate. By trial and error, we find that if $X_2 = 0.019$, the second term is equal to $0.0095 = 0.95\%$ of the first term.

Exercise 10.13. From the Maclaurin series for $\ln(1+x)$

$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \cdots$$

find the Taylor series for $1/(1+x)$, using the fact that

$$\frac{d[\ln(1+x)]}{dx} = \frac{1}{1+x}.$$

For what values of x is your series valid?

$$\frac{1}{1+x} = \frac{d}{dx}\left(x - \frac{1}{2}x^2 + \frac{1}{3}x^3 \cdots\right) = 1 - \frac{2x}{2} + \frac{3x^2}{3} - \frac{4x^3}{4} = 1 - x + x^2 - x^3 + x^4 - x^5 + \cdots$$

which is the series already obtained for $1/(1+x)$ in an earlier example. The series is invalid if $x \geqslant 1$.

Exercise 10.14. Find the formulas for the coefficients in a Taylor series that expands the function $f(x,y)$ around the point $x=a, y=b$.

$$f(x,y) = a_{00} + a_{10}(x-a) + a_{01}(y-b) + a_{11}(x-a)(y-b) + a_{21}(x-a)^2(y-b) + a_{12}(x-a)(y-b)^2 + \cdots$$

$$\begin{aligned} a_{00} &= f(a,b) \\ a_{10} &= \left(\frac{\partial f}{\partial y}\right)_x\Bigg|_{x=a,b=y} \\ a_{01} &= \left(\frac{\partial f}{\partial y}\right)_x\Bigg|_{a,b} \\ a_{11} &= \left(\frac{\partial^2 f}{\partial y \partial x}\right)\Bigg|_{a,b} \\ a_{mn} &= \frac{1}{n!m!}\left(\frac{\partial^{n+m} f}{\partial^m y \partial^n x}\right)\Bigg|_{a,b} \end{aligned}$$

PROBLEMS

1. Test the following series for convergence.

$$\sum_{n=0}^{\infty}((-1)^n(n-1)/n^2).$$

We apply the alternating series test:

$$\lim_{n\to\infty}|t_n| = \lim_{n\to\infty}\left(\frac{n-1}{n^2}\right) = \lim_{n\to\infty}\left(\frac{n}{n^2}\right) = \lim_{n\to\infty}\left(\frac{1}{n}\right) = 0$$

The series is convergent.

2. Test the following series for convergence.

$$\sum_{n=0}^{\infty}((-1)^n n/n!).$$

Note: $n! = n(n-1)(n-2)\cdots(2)(1)$ for positive integral values of n, and $0! = 1$. We apply the alternating series test:

$$\lim_{n\to\infty}|t_n| = \lim_{n\to\infty}\left(\frac{n}{n!}\right) = \lim_{n\to\infty}\left(\frac{1}{(n-1)!}\right) = 0$$

The series is convergent.

3. Test the following series for convergence.

$$\sum_{n=0}^{\infty}\left(1/n!\right).$$

Try the ratio test

$$r = \lim_{n\to\infty}\frac{a_{n+1}}{a_n} = \lim_{n\to\infty}\frac{n!}{(n+1)!} = \lim_{n\to\infty}\frac{1}{n+1} = 0$$

The series converges.

4. Find the Maclaurin series for $\cos(x)$.

$$\begin{aligned} a_0 &= \cos(0) = 1 \\ a_1 &= \frac{d}{dx}\cos(x)\Big|_0 = -\sin(0) = 0 \\ a_2 &= -\frac{1}{2!}\frac{d}{dx}\sin(x)\Big|_0 = -\frac{1}{2!}\cos(0) = -\frac{1}{2!} \end{aligned}$$

There is a repeating pattern. All of the odd-number coefficients vanish, and the even-number coefficients alternate between $1/n!$ and $-1/n!$.

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{1}{4!}x^4 - \frac{1}{6!}x^6 + \cdots$$

5. Find the Taylor series for $\cos(x)$, expanding about $x = \pi/2$.

$$\cos(x) = a_0 + a_1(x-\pi/2) + a_2(x-\pi/2)^2 + \cdots$$

$$\begin{aligned} a_0 &= \cos\left(\pi/2\right) = 0 \\ a_1 &= \frac{1}{1!}\frac{d}{dx}[\cos(x)]\Big|_{\pi/2} = -\frac{1}{2!}\sin(x)\Big|_{\pi/2} = -1 \\ a_2 &= \frac{1}{2!}\frac{d}{dx}[\cos(x)]\Big|_{\pi/2} = -\frac{1}{2!}\cos(x)\Big|_{\pi/2} = 0 \\ a_3 &= -\frac{1}{3!}\frac{d}{dx}[\cos(x)]\Big|_{\pi/2} = \frac{1}{3!}\sin(x)\Big|_{\pi/2} = \frac{1}{3!} \end{aligned}$$

There is a pattern, with all even-numbered coefficients vanishing and odd-numbered coefficients alternating between $1/n!$ and $-1/n!$.

$$\cos(x) = -\frac{1}{1!}(x-\pi/2) + \frac{1}{3!}(x-\pi/2)^3 - \frac{1}{5!}(x-\pi/2)^5 + \cdots$$

6. By use of the Maclaurin series already obtained in this chapter, prove the identity $e^{ix} = \cos(x) + i\sin(x)$.

$$\begin{aligned} e^{ix} &= 1 + \frac{1}{1!}ix + \frac{1}{2!}(ix)^2 + \frac{1}{3!}(ix)^3 + \frac{1}{4!}(ix)^4\cdots \\ &= 1 + \frac{i}{1!}x - \frac{1}{2!}(x)^2 - \frac{i}{3!}(x)^3 + \frac{1}{4!}(x)^4\cdots \\ \cos(x) + i\sin(x) &= 1 - \frac{x^2}{2!} + \frac{1}{4!}x^4 - \frac{1}{6!}x^6 + \cdots + i\left(x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7 + \cdots\right) \end{aligned}$$

$$= = 1 + \frac{i}{1!}x - \frac{1}{2!}(x)^2 - \frac{i}{3!}(x)^3 + \frac{1}{4!}(x)^4 + \frac{i}{5!}x^5 \cdots$$

a. Show that no Maclaurin series

$$f(x) = a_0 + a_1 x + a_2 x^2 + \cdots$$

can be formed to represent the function $f(x) = \sqrt{x}$. Why is this? The function is not analytic at $x = 0$. Its derivative is equal to $1/x$, which is infinite at $x = 0$.

b. Find the first few coefficients of the Maclaurin series for the function

$$f(x) = \sqrt{1+x}.$$

$$\begin{aligned}
\sqrt{1+x} &= (1+x)^{1/2} = a_0 + a_1 x + a_2 x^2 + \cdots \\
a_0 &= \sqrt{1-0} = 1 \\
a_1 &= \frac{1}{1!}\frac{d}{dx}(1+x)^{1/2}\Big|_0 \\
&= \frac{1}{2}\frac{1}{1!}(1+x)^{-1/2}\Big|_0 = \frac{1}{2} \\
a_2 &= \frac{1}{2!}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)\frac{d}{dx}(1+x)^{-1/2}\Big|_0 \\
&= -\frac{1}{4}\frac{1}{2!}(1+x)^{-3/2}\Big|_0 = -\frac{1}{8} \\
a_3 &= -\frac{1}{4}\frac{1}{3!}\frac{d}{dx}(1+x)^{-3/2}\Big|_0 \\
&= \frac{1}{4}\left(\frac{3}{2}\right)\frac{1}{3!}(1+x)^{-5/2}\Big|_0 = \frac{1}{16} \\
a_4 &= \frac{3}{8}\frac{1}{4!}\frac{d}{dx}(1+x)^{-5/2}\Big|_0 \\
&= -\frac{3}{8}\left(\frac{5}{2}\right)\frac{1}{4!}(1+x)^{-7/2}\Big|_0 = -\frac{5}{128} \\
\sqrt{1+x} &= 1 + \frac{x}{2} - \frac{x^2}{8} + \frac{x^3}{16} - \frac{5x^4}{128} + \cdots
\end{aligned}$$

7. Find the coefficients of the first few terms of the Taylor series

$$\sin(x) = a_0 + a_1\left(x - \frac{\pi}{4}\right) + a_2\left(x - \frac{\pi}{4}\right)^2 + \cdots$$

where x is measured in radians. What is the radius of convergence of the series?

$$\begin{aligned}
a_0 &= \sin(\pi/4) = \frac{1}{\sqrt{2}} = 0.717107 \\
a_1 &= \frac{1}{1!}\cos(x)\Big|_{\pi/4} = \frac{1}{\sqrt{2}} \\
a_2 &= -\frac{1}{2!}\sin(x)\Big|_{\pi/4} = -\frac{1}{2!\sqrt{2}} \\
a_3 &= \frac{1}{3!}\cos(x)\Big|_{\pi/4} = \frac{1}{3!\sqrt{2}}
\end{aligned}$$

The coefficients form a regular pattern:

$$a_n = -(-1)^n \frac{1}{n!\sqrt{2}}$$

$$\sin(x) = \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}}\left(x - \frac{\pi}{4}\right) + \frac{1}{2!\sqrt{2}}\left(x - \frac{\pi}{4}\right)^2 - \frac{1}{3!\sqrt{2}}\left(x - \frac{\pi}{4}\right)^3 + \cdots - (-1)^n \frac{1}{n!\sqrt{2}}\left(x - \frac{\pi}{4}\right)^n + \cdots$$

Since the function is analytic everywhere, the radius of convergence is infinite.

8. Find the coefficients of the first few terms of the Maclaurin series

$$\sinh(x) = a_0 + a_1 x + a_2 x^2 + \cdots$$

What is the radius of convergence of the series?

$$\begin{aligned}
\sinh(x) &= \frac{1}{2}\left[e^x - e^{-x}\right] \\
&= \frac{1}{2}\left[1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots - \left(1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \cdots\right)\right] \\
&= x + \frac{x^3}{3!} + \frac{x^5}{5!} + \frac{x^7}{7!} + \cdots
\end{aligned}$$

The function is analytic everywhere, so the radius of convergence is infinite.

9. The sine of $\pi/4$ radians (45°) is $\sqrt{2}/2 = 0.70710678\ldots$. How many terms in the series

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots$$

must be taken to achieve 1% accuracy at $x = \pi/4$?

$$\frac{\pi}{4} = 0.785398$$

$$x - \frac{x^3}{3!} = 0.785398 - 0.080746 = 0.704653$$

This is accurate to about 0.4%, so only two terms are needed.

10. The cosine of 30° ($\pi/6$) radians is equal to $\sqrt{3}/2 = 0.866025\cdots$. How many terms in the series

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$$

must be taken to achieve 0.1% accuracy $x = \pi/6$?

$$1 - \frac{x^2}{2!} = 1 - 0.137078 = 0.8629$$

This is accurate to about 0.4%.

$$1 - \frac{x^2}{2!} + \frac{x^4}{4!} = 1 - 0.137078 + 0.003132 = 0.866154$$

This is accurate to about 0.003%. Three terms must be included.

11. Estimate the largest value of x that allows e^x to be approximated to 1% accuracy by the following partial sum

$$e^x \approx 1 + x.$$

Here is a table of values:

a. •	*x difference*	1 + *x*	e^x	%
•	0.20000	1.20000	1.221402758	1.78
•	0.19000	1.19000	1.209249598	1.62
•	0.18000	1.18000	1.197217363	1.46
•	0.17000	1.17000	1.185304851	1.31
•	0.15000	1.15000	1.161834243	1.03
•	0.14000	1.14000	1.150273799	0.90
•	0.14500	1.14500	1.156039570	0.96
•	0.14777	1.14777	1.159246239	0.9999
•	By trial and error, 1% accuracy is obtained with $x \prec 0.14777$.			

12. Estimate the largest value of x that allows e^x to be approximated to 0.01% accuracy by the following partial sum

$$e^x \approx 1 + x + \frac{x^2}{2!}.$$

Here is a table of values, calculated with Excel:

x	1 + *x*	e^x	*% difference*
0.1000	1.1050000	1.105170918	0.015467699
0.2000	1.2200000	1.221402758	0.114980177
0.0900	1.0940500	1.094174284	0.011359966
0.0800	1.0832000	1.083287068	0.008038005
0.0850	1.0886125	1.088717067	0.009605502
0.0860	1.0896980	1.089806328	0.009941131
0.0870	1.0907845	1.090896680	0.010284315
0.0869	1.0906758	1.090787596	0.010249655
0.0868	1.0905671	1.090678522	0.010215070
0.0865	1.0902411	1.090351368	0.010111774
0.0864	1.0901325	1.090242338	0.010077494
0.0863	1.0900238	1.090133319	0.010043289
0.0862	1.0899152	1.090024311	0.010009161
0.0861	1.0898066	1.089915314	0.009975108
By trial and error, 0.01% accuracy is obtained with $x \prec 0.0861$.			

13. Find two different Taylor series to represent the function

$$f(x) = \frac{1}{x}$$

such that one series is

$$f(x) = a_0 + a_1(x-1) + a_2(x-1)^2 + \cdots$$

and the other is

$$f(x) = b_0 + b_1(x-2) + b_3(x-2)^2 + \cdots$$

Show that $b_n = a_n/2^n$ for any value of n. Find the interval of convergence for each series (the ratio test may be used). Which series must you use in the vicinity of $x = 3$? Why? Find the Taylor series in powers of $(x-10)$ that represents the function $\ln(x)$.

$$\frac{1}{x} = a_0 + a_1(x-1) + a_2(x-1)^2 + \cdots$$

$$a_0 = \frac{1}{1} = 1$$

$$a_1 = -\left.\frac{1}{x^2}\right|_1 = -1$$

$$a_2 = \frac{1}{2!}\left.\left(\frac{2}{x^3}\right)\right|_1 = 1$$

$$a_3 = -\frac{1}{2!}\left.\left(\frac{6}{x^4}\right)\right|_1 = 1$$

The coefficients follow a regular pattern so that

$$a_n = (-1)^n \frac{1}{x} = 1 - (x-1) + (x-1)^2 - (x-1)^3 + (x-1)^4 + \cdots$$

The function is not analytic at $x = 0$, so the interval of convergence is $0 \prec x \prec 2$

$$\frac{1}{x} = b_0 + b_1(x-2) + b_2(x-2)^2 + \cdots$$
$$b_0 = \frac{1}{2} = \frac{1}{2}$$
$$b_1 = -\frac{1}{x^2}\bigg|_2 = -\frac{1}{4}$$
$$b_2 = \frac{1}{2!}\left(\frac{2}{x^3}\right)\bigg|_2 = \frac{1}{8}$$
$$b_3 = -\frac{1}{2!}\left(\frac{6}{x^4}\right)\bigg|_2 = -\frac{1}{16}$$

The coefficients follow a regular pattern so that

$$b_n = (-1)^n \frac{1}{2^n} = \frac{a_n}{2^n}$$
$$\frac{1}{x} = \frac{1}{2} - \frac{1}{4}(x-1) + \frac{1}{8}(x-1)^2 - \frac{1}{16}(x-1)^3 + \frac{1}{32}(x-1)^4 + \cdots$$

The function is not analytic at $x = 0$, so the interval of convergence is $0 \prec x \prec 4$. The second series must be used for $x = 3$, since this value of x is outside the region of convergence of the first series.

14. Find the Taylor series in powers of $(x-5)$ that represents the function $\ln(x)$.

$$\ln(x) = \ln(5) + \frac{1}{1!}\frac{d}{dx}\ln(x)\bigg|_5 + \cdots + \frac{1}{n!}\frac{d^n}{dx^n}\ln(x)\bigg|_5 + \cdots$$
$$\frac{d}{dx}\ln(x)\bigg|_{x=5} = \frac{1}{x}\bigg|_{x=5} = \frac{1}{5}$$

The derivatives follow a regular pattern:

$$\left(\frac{d^n f}{dx^n}\right)_{x=1} = (-1)^{n-1}\frac{(n-1)!}{x^n}\bigg|_{x=5} = \frac{(-1)^{n-1}(n-1)!}{5^n}$$
$$a_n = \frac{(-1)^{n-1}(n-1)!}{n!5^n} = \frac{(-1)^{n-1}}{n5^n}$$
$$\ln(x) = \ln(5) + \frac{1}{5}x - \frac{1}{50}x^2 + \frac{1}{375}x^3 - \frac{1}{2500}x^4 + \cdots$$

15. Using the Maclaurin series for e^x, show that the derivative of e^x is equal to e^x.

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots$$
$$\frac{d}{dx}e^x = 0 + 1 + \frac{2x}{2!} + \frac{3x^2}{3!} + \frac{4x^3}{4!} + \cdots = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots = e^x$$

16. Find the Maclaurin series that represents $\cosh(x)$. What is its radius of convergence?

$$\cosh(x) = \frac{1}{2}(e^x + x^{-x}) = \frac{1}{2}\left(1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots + 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots\right)$$
$$= \frac{1}{2}\left(2 + 2\frac{x^2}{2!} + 2\frac{x^4}{4!} + \cdots\right)$$
$$= 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \frac{x^6}{6!} + \cdots$$

Apply the ratio test:

$$r = \lim_{n\to\infty}\frac{a_{n+1}}{a_n} = \lim_{n\to\infty}\frac{x^{2n}/(2n)!}{x^{2n-2}/(2n-2)!}$$
$$= \lim_{n\to\infty}\frac{x^2(2n-2)!}{/(2n)!}$$
$$= \lim_{n\to\infty}\frac{x^2}{(2n)(2n-1)} = 0$$

The series converges for any finite value of x.

17. Find the Taylor series for $\sin(x)$, expanding around $\pi/2$.

$$\sin(x) = a_0 + a_1(x-\pi/2) + a_2(x-\pi/2)^2 + a_3(x-\pi/2)^3 + \cdots$$
$$a_0 = \sin(\pi/2) = 1$$
$$a_n = \frac{1}{n!}\frac{d^n}{dx^n}\sin(x)\bigg|_{\pi/2}$$
$$\frac{df}{dx} = \cos(x)$$
$$a_1 = \cos(\pi/2) = 0$$
$$\frac{d^2 f}{dx^2} = -\sin(x)$$
$$a_2 = -\frac{1}{2!}\sin(\pi/2) = -\frac{1}{2!}$$
$$\frac{d^3 f}{dx^3} = -\cos(x)$$
$$a_3 = -\frac{1}{3!}\cos(\pi/2) = 0$$
$$\frac{d^4 f}{dx^4} = \sin(x)$$
$$a_4 = \frac{1}{4!}\sin(\pi/2) = \frac{1}{4!}$$

There is a pattern. Only even values of n occur,and signs alternate.

$$\sin(x) = 1 - \frac{1}{2!}(x-\pi/2)^2 + \frac{1}{4!}(x-\pi/2)^4 - \frac{1}{6!}(x-\pi/2)^6 + \cdots$$

18. Find the interval of convergence for the series for $\sin(x)$.

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7 + \cdots$$

Apply the alternating series test. Each term is smaller than the previous term if x is finite and if you go far enough into the series. The series converges for all finite values of x.

19. Find the interval of convergence for the series for $\cos(x)$.

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$$

Apply the alternating series test. Each term is smaller than the previous term if x is finite and if you go far enough into the series. The series converges for all finite values of x.

20. Prove the following fact about power series: If two power series in the same independent variable are equal to each other for all values of the independent variable, then any coefficient in one series is equal to the corresponding coefficient of the other series.

$$a_0+a_1x+a_2x^2+a_3x^3\cdots = b_0+b_1x+b_2x^2+b_3x^3+\cdots$$

Since this equality is valid for all values of x, it is value for $x = 0$:

$$a_0 = b_0$$

Since all derivatives are assume to exist, take the first derivative:

$$a_1 + 2a_2x + 3a_3x^2 + \cdots = b_1 + 2b_2x + 3b_3x^2 + \cdots$$

This must be valid for $x = 0$

$$a_1 = b_1$$

Take the second derivative

$$2a_2 + 6a_3x + \cdots = 2b_2 + 6b_3x + \cdots$$

This must be valid for $x = 0$

$$a_2 = b_2$$

Continue with more derivatives, setting each derivative equal to its value for $x = 0$. The result is that, for every value of $n \succeq 0$:

$$a_n = b_n$$

21. Using the Maclaurin series, show that

$$\int_0^{x_1} e^s \mathrm{d}x = e^x\Big|_0^{x_1} = e^{x_1} - 1$$

$$\begin{aligned}
\int_0^{x'} e^s \mathrm{d}x &= \int_0^{x'}\left(1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots\right)\mathrm{d}x \\
&= \left(x + \frac{x^2}{2} + \frac{x^3}{(3)2!} + \frac{x^4}{(4)3!} + \cdots\right)\Bigg|_0^{x_1} \\
&= 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots - 1 \\
&= e^{x_1} - 1
\end{aligned}$$

22. Using the Maclaurin series, show that

$$\int_0^{x_1} \cos(ax)\mathrm{d}x = \frac{1}{a}\sin(x)\Bigg|_0^{x_1} = \frac{1}{a}\sin(ax_1)$$

$$\begin{aligned}
&\int_0^{x_1} \cos(ax)\mathrm{d}x \\
&= \int_0^{x_1}\left(1 - \frac{(ax)^2}{2!} + \frac{(ax)^4}{4!} - \frac{(ax)^6}{6!} + \cdots\right)\mathrm{d}x \\
&= \left(x - \frac{a^2x^3}{(3)2!} + \frac{a^4x^5}{(5)4!} - \frac{a^6x^7}{(7)6!} + \cdots\right)\Bigg|_0^{x_1} \\
&= \frac{1}{a}\left(ax - \frac{a^3x^3}{3!} + \frac{a^5x^5}{5!} - \frac{a^7x^7}{7!} + \cdots\right)\Bigg|_0^{x_1} \\
&= \frac{1}{a}\sin(ax_1)
\end{aligned}$$

23. Find the first few terms of the two-variable Maclaurin series representing the function

$$f(x,y) = \sin(x+y)$$

$$\begin{aligned}
f(0,0) &= \sin(0) = 0 \\
\left(\frac{\partial f}{\partial x}\right)_y\Bigg|_{0,0} &= \cos(x+y)|_{0,0} = 1 \\
\left(\frac{\partial f}{\partial y}\right)_x\Bigg|_{0,0} &= \cos(x+y)|_{0,0} = 1 \\
\left(\frac{\partial^2 f}{\partial y\partial x}\right)\Bigg|_{0,0} &= -\sin(x+y)|_{0,0} = 1 \\
\left(\frac{\partial^2 f}{\partial x^2}\right)\Bigg|_{0,0} &= -\sin(x+y)|_{0,0} = 0 \\
\left(\frac{\partial^2 f}{\partial y^2}\right)\Bigg|_{0,0} &= -\sin(x+y)|_{0,0} = 0 \\
\left(\frac{\partial^3 f}{\partial y\partial x^2}\right)\Bigg|_{0,0} &= -\big(\cos(x+y)\big)\big|_{0,0} = -1
\end{aligned}$$

$$\left(\frac{\partial^3 f}{\partial y^2 \partial x}\right)\bigg|_{0,0} = -\left(\cos(x+y)\right)\big|_{0,0} = -1$$
$$\left(\frac{\partial^4 f}{\partial y^2 \partial x^2}\right)\bigg|_{0,0} = \left(\sin(x+y)\right)\big|_{0,0} = 0$$
$$\left(\frac{\partial^5 f}{\partial y^2 \partial x^3}\right)\bigg|_{0,0} = \left(\cos(x+y)\right)\big|_{0,0} = 1$$

There is a pattern. If $n+m$ is even, the derivative vanishes. If $n+m$ is odd, the derivative has magnitude 1 with alternating signs.

$$\sin(x+y) = x + y - \frac{1}{1!2!}(x^2y + xy^2) + \frac{1}{3!2!}(x^2y^3 + x^3y^2) - \frac{1}{3!4!}(x^4y^3 + x^3y^4) + \cdots$$

24. Find the first few terms of the two-variable Taylor series:

$$\ln(xy) = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} a_{mn}(x-1)^n(y-1)^m$$

$$f(1,1) = \ln(1) = 0$$

$$\left(\frac{\partial f}{\partial x}\right)_y\bigg|_{0,0} = \frac{y}{xy}\bigg|_{1,1} = \frac{1}{x}\bigg|_{1,1} = 1$$
$$\left(\frac{\partial f}{\partial y}\right)_x\bigg|_{0,0} = \frac{x}{xy}\bigg|_{1,1} = \frac{1}{y}\bigg|_{1,1} = 1$$

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right)\bigg|_{1,1} = \left(\frac{\partial^2 f}{\partial y \partial x}\right)\bigg|_{1,1} = 0$$

$$\left(\frac{\partial^2 f}{\partial x^2}\right)\bigg|_{1,1} = -\frac{1}{x^2}\bigg|_{1,1} = -1$$
$$\left(\frac{\partial^2 f}{\partial y^2}\right)\bigg|_{1,1} = -\frac{1}{y^2}\bigg|_{1,1} = -1$$
$$\left(\frac{\partial^3 f}{\partial x^3}\right)\bigg|_{1,1} = 2\frac{1}{y^3}\bigg|_{1,1} = 2$$

There is a pattern: All of the mixed derivatives vanish.

$$\left(\frac{\partial^n f}{\partial x^n}\right)\bigg|_{1,1} = \left(\frac{\partial^n f}{\partial x^n}\right)\bigg|_{1,1} = -(-1)^n(n-1)!$$

The series is

$$\ln(xy) = 1 + 1 - (x-1) - (y-1) + \frac{1}{2}[(x-1)^2 + (y-1)^2] - \frac{1}{3}$$

This is the same as the sum of the two series

$$\ln(x) = (x-1) - \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 - \frac{1}{4}(x-1)^4 + \cdots$$
$$\ln(x) = (y-1) - \frac{1}{2}(y-1)^2 + \frac{1}{3}(y-1)^3 - \frac{1}{4}(y-1)^4 + \cdots$$

This could have been deduced from the fact that

$$\ln(xy) = \ln(x) + \ln(y)$$

Chapter 11

Functional Series and Integral Transforms

EXERCISES

Exercise 11.1. Using trigonometric identities, show that the basis functions in the series in Eq. (11.1) are periodic with period $2L$.

We need to show for arbitrary n that

$$\sin\left[\frac{n\pi(x+2L)}{L}\right] = \sin\left(\frac{n\pi x}{L}\right)$$

and

$$\cos\left[\frac{n\pi(x+2L)}{L}\right] = \cos\left(\frac{n\pi x}{L}\right)$$

From a trigonometric identity

$$\begin{aligned}\sin\left[\frac{n\pi(x+2L)}{L}\right] &= \sin\left[\frac{n\pi(x)}{L}\right]\cos[2n\pi] \\ &\quad + \cos\left[\frac{n\pi(x)}{L}\right]\sin(2n\pi) \\ &= \sin\left[\frac{n\pi(x)}{L}\right]\end{aligned}$$

This result follows from the facts that

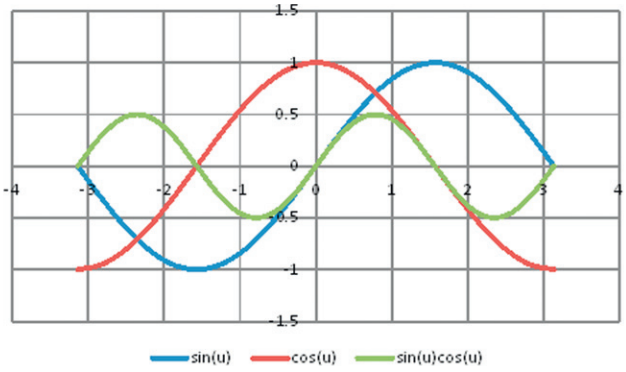
$$\begin{aligned}\cos[2n\pi] &= 1 \\ \sin(2n\pi) &= 0\end{aligned}$$

Similarly,

$$\begin{aligned}\cos\left[\frac{n\pi(x+2L)}{L}\right] &= \cos\left[\frac{n\pi(x)}{L}\right]\cos[2n\pi] \\ &\quad + \sin\left[\frac{n\pi(x)}{L}\right]\sin(2n\pi) \\ &= \cos\left[\frac{n\pi(x)}{L}\right]\end{aligned}$$

Exercise 11.2. Sketch a rough graph of the product $\cos\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)$ from 0 to 2π and convince yourself that its integral from $-L$ to L vanishes. For purposes of the graph, we let $u = x/L$, so that we plot from $-\pi$ to π.

Here is an accurate graph showing the sine, the cosine, and the product. It is apparent that the negative area of the product cancels the positive area.



Exercise 11.3. Show that Eq. (11.15) is correct.

$$\begin{aligned}\int_{-L}^{L} f(x)\sin\left(\frac{m\pi x}{L}\right)\mathrm{d}x &= \sum_{n=0}^{\infty} a_n \int_{-L}^{L}\cos\left(\frac{n\pi x}{L}\right) \\ &\quad \times \sin\left(\frac{m\pi x}{L}\right)\mathrm{d}x \\ &\quad + \sum_{n=0}^{\infty} b_n \int_{-L}^{L}\sin\left(\frac{n\pi x}{L}\right) \\ &\quad \times \sin\left(\frac{m\pi x}{L}\right)\mathrm{d}x\end{aligned}$$

By orthogonality, all of the integrals vanish except the integral with two sines and $m = n$. This integral equals L.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00035-5

$$\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x = b_n L$$

$$b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

Exercise 11.4. Show that the a_n coefficients for the series representing the function in the previous example all vanish.

$$a_0 = \frac{1}{2L}\int_{-L}^{L} x\mathrm{d}x = \left.\frac{x^2}{2}\right|_{-L}^{L} = 0$$

$$a_n = \frac{1}{L}\int_{-L}^{L} x\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

Integrate by parts: Let $u = x$, $\mathrm{d}u = \mathrm{d}x$, $\mathrm{d}v = (\mathrm{d}v/\mathrm{d}x)\mathrm{d}x = \cos(n\pi x/L)\mathrm{d}x$, $v = (L/n\pi)\sin(n\pi x/L)$

$$\int u\mathrm{d}v = uv - \int v\mathrm{d}u$$

$$\begin{aligned}\int_{-L}^{L} x\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x &= x\left(\frac{L}{n\pi}\right)\sin(n\pi x/L)\Big|_{-L}^{L} \\ &\quad - \left(\frac{L}{n\pi}\right)\int_{-L}^{L}\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x \\ &= \left(\frac{L}{n\pi}\right)[n\pi\sin(n\pi) \\ &\quad - n\pi\sin(-n\pi)] \\ &\quad + \left(\frac{L}{n\pi}\right)(\cos\left(\frac{n\pi x}{L}\right)\Big|_{-L}^{L} \\ &= 0 + \left(\frac{L}{n\pi}\right)[\cos(n\pi) \\ &\quad - \cos(-n\pi)] = 0\end{aligned}$$

Exercise 11.5. Find the Fourier cosine series for the even function

$$f(x) = |x| \quad \text{for} - L < x < L.$$

Sketch a graph of the periodic function that is represented by the series. This is an even function, so the b coefficients vanish.

$$a_0 = \frac{1}{2L}\int_{-L}^{L}|x|\mathrm{d}x = \frac{1}{L}\int_0^L x\mathrm{d}x = \frac{1}{L}\left.\frac{x^2}{2}\right|_0^L = \frac{L}{2}$$

For $n \geqslant 1$,

$$a_n = \frac{1}{L}\int_{-L}^{L}|x|\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \frac{2}{L}\int_0^L x\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

$$\begin{aligned}\int_0^L x\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x &= x\left(\frac{L}{n\pi}\right)\sin(n\pi x/L)\Big|_0^L \\ &\quad - \left(\frac{L}{n\pi}\right)\int_0^L\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x \\ &= \left(\frac{L}{n\pi}\right)[n\pi\sin(n\pi) - n\pi \\ &\quad \sin(0)] + \left(\frac{L}{n\pi}\right)(\cos\left(\frac{n\pi x}{L}\right)\Big|_0^L \\ &= 0 + \left(\frac{L}{n\pi}\right)[\cos(n\pi) - \cos(0)] \\ &= \left(\frac{L}{n\pi}\right)[(-1)^n) - 1]\end{aligned}$$

$$\begin{aligned}|x| &= \frac{L}{2} + \sum_{n-1}^{\infty}\left(\frac{L}{n\pi}\right)[(-1)^n) - 1] \\ &\quad \times\cos\left(\frac{n\pi x}{L}\right)\end{aligned}$$

Exercise 11.6. Derive the orthogonality relation expressed above.

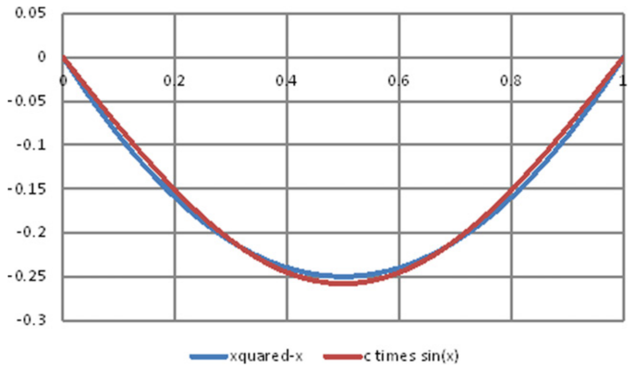
$$\begin{aligned}&\int_{-L}^{L}\exp\left(\frac{im\pi x}{L}\right)^*\exp\left(\frac{in\pi x}{L}\right)\mathrm{d}x \\ &= \int_{-L}^{L}\left[\cos\left(\frac{m\pi x}{L}\right) - i\sin\left(\frac{m\pi x}{L}\right)\right] \\ &\quad \left[\cos\left(\frac{n\pi x}{L}\right) + i\sin\left(\frac{n\pi x}{L}\right)\right]\mathrm{d}x \\ &= \int_{-L}^{L}\cos\left(\frac{m\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x \\ &\quad - i\int_{-L}^{L}\times\sin\left(\frac{m\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x \\ &\quad + i\int_{-L}^{L}\cos\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x \\ &\quad + \int_{-L}^{L}\sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x \\ &= \delta_{mn}L - i\times 0 + i\times 0 + \delta_{mn}L = 2\delta_{mn}L\end{aligned}$$

We have looked up the integrals in the table of definite integrals.

Exercise 11.7. Construct a graph with the function f from the previous example and $c_1\psi_1$ on the same graph. Let $a = 1$ for your graph. Comment on how well the partial sum with one term approximates the function.

$$f = x^2 - x \approx -0.258012\sin(\pi x)$$

Here is the graph, constructed with Excel:



Exercise 11.8. Find the Fourier transform of the function $f(x) = e^{-|x|}$. Since this is an even function, you can use the one-sided cosine transform.

$$F(k) = \sqrt{\frac{2}{\pi}} \int_0^\infty e^{-x} \cos(kx)\mathrm{d}x$$

This integral is found in the table of definite integrals:

$$F(k) = \sqrt{\frac{2}{\pi}} \int_0^\infty e^{-x} \cos(kx)\mathrm{d}x = \sqrt{\frac{2}{\pi}} \frac{1}{1+k^2}$$

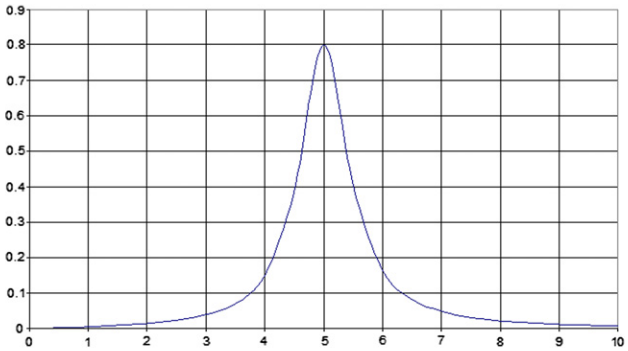
Exercise 11.9. Repeat the calculation of the previous example with $a = 0.500\ \mathrm{s}^{-1}$, $b = 5.00\ \mathrm{s}^{-1}$ Show that a narrower line width occurs.

The Fourier transform is:

$$F(\omega) = \frac{2}{\sqrt{\pi}} \frac{2ab\omega}{[a^2 + (b-\omega)^2][a^2 + (b+\omega)^2]}$$

$$F(\omega) = \frac{2}{\sqrt{\pi}} \frac{(5.00\ \mathrm{s}^{-2})\omega}{[0.250\ \mathrm{s}^{-2} + (5.00\ \mathrm{s}^{-1} - \omega)^2][0.250\ \mathrm{s}^{-2} + (5.00\ \mathrm{s}^{-1} + \omega)^2]}$$

Here is the graph of the transform, ignoring a constant factor:



Exercise 11.10. Find the Laplace transform of the function $f(t) = e^{at}$ where a is a constant.

$$F(s) = \int_0^\infty e^{at}e^{-st}\,\mathrm{d}t = \int_0^\infty e^{(a-s)t}\,\mathrm{d}t$$
$$= \frac{1}{a-s} e^{(a-s)t}\Big|_0^\infty$$

If $a - s \prec 0$,

$$F(s) = \frac{1}{a-s}(0-1) = \frac{1}{s-a}$$

as shown in Table 11.1. If $a - s \geqslant 0$, the integral diverges and the Laplace transform is not defined.

Exercise 11.11. Derive the version of Eq. (11.49) for $n = 2$. Apply the derivative theorem to the first derivative

$$\begin{aligned} \mathcal{L}\{\mathrm{d}^2 f/\mathrm{d}t^2\} &= \mathcal{L}\{f^{(2)}\} = s\mathcal{L}\{f^{(1)}\} - f^{(1)}(0) \\ &= s[s\mathcal{L}\{f\} - f'(0)] - f^{(1)}(0) \\ &= s^2\mathcal{L}\{f\} - sf'(0) - f^{(1)}(0) \end{aligned}$$

Exercise 11.12. Find the Laplace transform of the function

$$f(t) = t^n e^{at}.$$

where n is an integer.

$$F(s) = \int_0^\infty t^n e^{(a-s)t}\mathrm{d}t = \int_0^\infty t^n e^{-bt}$$
$$\mathrm{d}t = \frac{1}{b^{n+1}} \int_0^\infty u^n e^u \mathrm{d}u = \frac{n!}{b^{n+1}} = \frac{n!}{(s-a)^{n+1}}$$

where $b = s - a$ and where $u = bt$ and where we have used Eq. (1) of Appendix F.

Exercise 11.13. Find the inverse Laplace transform of

$$\frac{1}{s(s^2+k^2)}.$$

We recognize $k/(s^2+k^2)$ as the Laplace transform of $\cos(kt)$, so that

$$\frac{1}{s^2+k^2} = \mathcal{L}\left\{\frac{\cos(kt)}{k}\right\}$$

From the integral theorem

$$\mathcal{L}\left\{\frac{1}{k}\int_0^t \cos(ku)\mathrm{d}u\right\} = \mathcal{L}\left\{\frac{1}{k^2}\sin(kt)\right\}$$
$$= \frac{1}{s}\mathcal{L}\left\{\frac{\cos(kt)}{k}\right\} = \frac{1}{ks(s^2+k^2)}$$
$$\mathcal{L}\left\{\frac{1}{k}\sin(kt)\right\} = \frac{1}{s(s^2+k^2)}$$
$$\mathcal{L}^{-1}\left\{\frac{1}{s(s^2+k^2)}\right\} = \frac{1}{k}\sin(kt)$$

PROBLEMS

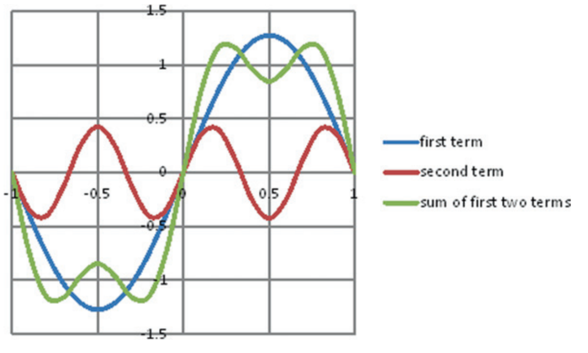
1. Find the Fourier series that represents the square wave

$$A(t) = \begin{cases} -A_0 & -T < t < 0 \\ A_0 & 0 < t < T, \end{cases}$$

where A_0 is a constant and T is the period. Make graphs of the first two partial sums. This is an odd function, so we will have a sine series:

$$\begin{aligned} a_n &= 0 \\ b_n &= \frac{1}{T}\int_{-T}^{T} f(t)\sin\left(\frac{n\pi t}{T}\right)dt = -\frac{A_0}{T} \\ &\quad\times\int_{-T}^{0}\sin\left(\frac{n\pi t}{T}\right)dt + \frac{A_0}{T}\int_{0}^{T}\sin\left(\frac{n\pi t}{T}\right)dt \\ &= -\frac{A_0}{T}\left(\frac{T}{n\pi}\right)\int_{-n\pi}^{0}\sin(u)du + \frac{A_0}{T}\left(\frac{T}{n\pi}\right) \\ &\quad\times\int_{0}^{n\pi}\sin(u)du \\ &= \frac{A_0}{n\pi}[\cos(0)-\cos(-n\pi)] - \frac{A_0}{n\pi} \\ &\quad\times[\cos(n\pi)-\cos(0)] \\ &= \frac{2A_0}{n\pi}[\cos(0)-\cos(n\pi)] = \frac{2A_0}{n\pi}[1-(-1)^n] \\ A(t) &= \sum_{n=1}^{\infty}\frac{2A_0}{n\pi}[1-(-1)^n]\sin\left(\frac{n\pi t}{T}\right) \\ &= \frac{4A_0}{\pi}\sin\left(\frac{\pi t}{T}\right) + \frac{4A_0}{3\pi}\sin\left(\frac{3\pi t}{T}\right) + \cdots \end{aligned}$$

where we have let $u = n\pi t/T$ and $dt = (T/n\pi)du$ and have used the fact that the cosine is an even function. Here is a graph that shows the first term (the first partial sum), the second term, and the sum of these two terms (the second partial sum):



For the graph, we have let A_0 equal unity.

2. Find the Fourier series to represent the function

$$f(x) = \begin{matrix} -1 & \text{if } -L \prec x \prec -L/2 \\ 1 & \text{if } -L/2 \prec x \prec L/2 \\ -1 & \text{if } L/2 \prec x \prec L \end{matrix}$$

Construct a graph showing the first three terms of the series and the third partial sum. This is an even function, so the Fourier series will be a cosine series.

$$\begin{aligned} a_0 &= \frac{1}{2L}\int_{-L}^{L} f(x)dx = \frac{1}{2L}\int_{-L}^{-L/2}(-1)dx \\ &\quad+\frac{1}{2L}\int_{-L/2}^{L/2}(1)dx\frac{1}{2L}\int_{L/2}^{L}(-1)dx \\ &= \frac{1}{2L}\left(-\frac{L}{2}+L-\frac{L}{2}\right) = 0 \\ a_n &= \frac{1}{L}\int_{-L}^{L} f(x)\cos\left(\frac{n\pi x}{L}\right)dx = \frac{1}{L}\int_{-L}^{-L/2}(-1) \\ &\quad\times\cos\left(\frac{n\pi x}{L}\right)dx + \frac{1}{L}\int_{-L/2}^{L/2}(1)\cos\left(\frac{n\pi x}{L}\right)dx \\ &\quad\times\frac{1}{L}\int_{L/2}^{L}(-1)\cos\left(\frac{n\pi x}{L}\right)dx \\ u &= \frac{n\pi x}{L};\ du = \frac{n\pi}{L}dx;\ x = \frac{Lu}{n\pi};\ dx = \frac{L}{n\pi}du \\ a_n &= \frac{1}{L}\left(\frac{L}{n\pi}\right)\left[\int_{-n\pi}^{-n\pi/2}(-1)\cos(u)du\right. \\ &\quad\left.+\int_{-n\pi/2}^{n\pi/2}(1)\cos(u)du+\int_{n\pi/2}^{n\pi}(-1)\cos(u)du\right] \\ &= \left(\frac{1}{n\pi}\right)\left[-\sin\left(\frac{-n\pi}{2}\right)+\sin(-n\pi)+\sin\left(\frac{n\pi}{2}\right)\right. \\ &\quad\left.-\sin\left(\frac{-n\pi}{2}\right)-\sin(n\pi)+\sin\left(\frac{n\pi}{2}\right)\right] \end{aligned}$$

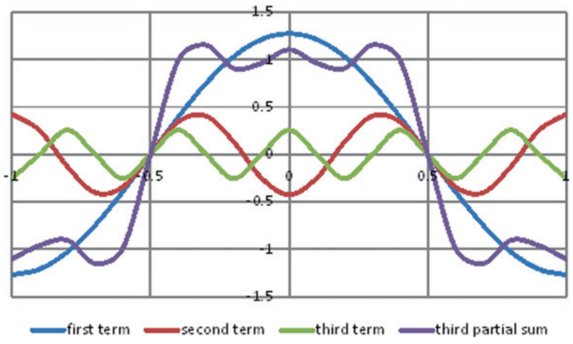
We use the fact the sine is an odd function:

$$\begin{aligned} a_n &= \left(\frac{1}{n\pi}\right)\left[\sin\left(\frac{n\pi}{2}\right)+0+\sin\left(\frac{n\pi}{2}\right)+\sin\left(\frac{n\pi}{2}\right)\right. \\ &\quad\left.-0+\sin\left(\frac{n\pi}{2}\right)\right] = \left(\frac{1}{n\pi}\right)\left[4\sin\left(\frac{n\pi}{2}\right)\right] \end{aligned}$$

$\sin(n\pi/2)$ follows the pattern 0,1,0, $-$ 1,0,1,0, $-$ 1, ... so that the even values of n produce vanishing terms. The Fourier series is

$$\begin{aligned} f(x) &= \left(\frac{4}{\pi}\right)\cos\left(\frac{\pi x}{L}\right) - \left(\frac{4}{3\pi}\right)\cos\left(\frac{3\pi x}{L}\right) \\ &\quad+\left(\frac{4}{5\pi}\right)\cos\left(\frac{5\pi x}{L}\right) - \cdots \end{aligned}$$

The following graph shows the first three terms and the third partial sums. For this graph, we have let $L = 1$.



Note that we have the typical overshoot at the discontinuity in the function.

3. Find the Fourier series to represent the function

$$A(t) = \begin{cases} e^{-|x/L|} & -L < t < L \\ 0 & \text{elsewhere} \end{cases}$$

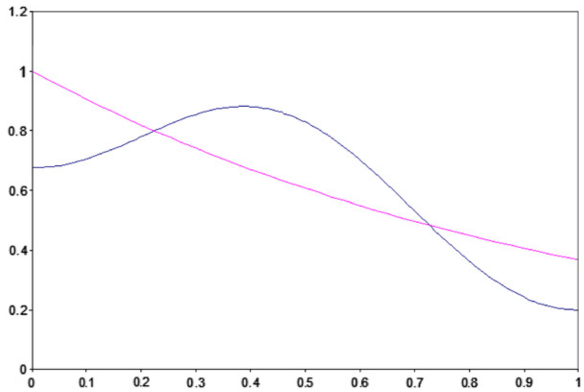
Your series will be periodic and will represent the function only in the region $-L < t < L$. Since the function is even, the series will be a cosine series.

$$a_0 = \frac{1}{2L}\int_{-L}^{L} f(x)\mathrm{d}x = \frac{1}{L}\int_0^L e^{-x/L}\mathrm{d}x$$
$$= -\left.e^{-x/L}\right|_0^L = -(e^{-1}-1) = (1-e^{-1})$$
$$= 0.6321206$$
$$a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$
$$= \frac{2}{L}\int_0^L e^{-x/L}\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$
$$u = \frac{n\pi x}{L};\quad x = \frac{Lu}{n\pi};\quad \mathrm{d}x = \left(\frac{L}{n\pi}\mathrm{d}u\right)$$
$$a_n = \frac{2}{L}\left(\frac{L}{n\pi}\right)\int_0^{n\pi}\exp\left(-\frac{u}{n\pi}\right)\cos(u)\mathrm{d}u$$
$$= \left(\frac{2}{n\pi}\right)\left[\frac{\exp(-u/n\pi)}{\left(\frac{1}{n\pi}\right)^2+1}\right.$$
$$\times\left.\left[\left(\frac{-1}{n\pi}\right)\cos(u)+\sin(u)\right]\right]\Bigg|_0^{n\pi}$$

where we have used Eq. (50) of Appendix E.

$$a_n = \left(\frac{2}{n\pi}\right)\left[\frac{\exp(-1)}{\left(\frac{1}{n\pi}\right)^2+1}\left[\left(\frac{1}{n\pi}\right)\cos(n\pi)\right.\right.$$
$$\left.\left.+\sin(n\pi)\right]\right]$$
$$-\left(\frac{2}{n\pi}\right)\left[\frac{\exp(-0)}{\left(\frac{1}{n\pi}\right)^2+1}\left[\left(\frac{-1}{n\pi}\right)\cos(0)\right.\right.$$
$$\left.\left.+\sin(0)\right]\right]$$
$$= \left(\frac{2}{n^2\pi^2}\right)\left[\frac{\exp(-1)}{\left(\frac{1}{n\pi}\right)^2+1}\left[\left(\frac{-1}{n\pi}\right)-(-1)^n\right]\right]$$
$$+\left(\frac{2}{n\pi}\right)\left[\frac{1}{\left(\frac{1}{n\pi}\right)^2+1}\left(\frac{1}{n\pi}\right)\right]$$
$$= \left(\frac{2}{n^2\pi^2}\right)\left[\frac{(-1)^{n+1}e^{-1}+1}{\left(\frac{1}{n\pi}\right)^2+1}\right]$$
$$a_1 = \left(\frac{1}{\pi^2}\right)\left[\frac{e^{-1}+1}{\frac{1}{\pi^2}+1}\right] = 0.1258445$$
$$a_2 = \left(\frac{1}{4\pi^2}\right)\left[\frac{-e^{-1}+1}{\frac{1}{\pi^2}+1}\right] = 0.1115872$$
$$f(x) = (1-e^{-L}) + \sum_{n=1}^{\infty}\left(\frac{2}{n^2\pi^2}\right)$$
$$\times\left[\frac{(-1)^{n+1}e^{-1}-1}{\left(\frac{1}{n\pi}\right)^2+1}\right]\cos\left(\frac{n\pi x}{L}\right)$$
$$= 0.6321206 + \left(\frac{2}{\pi^2}\right)\left[\frac{-e^{-1}-1}{\left(\frac{1}{\pi}\right)^2+1}\right]\cos\left(\frac{\pi x}{L}\right)$$
$$+\left(\frac{2}{\pi^2}\right)\left[\frac{e^{-1}-1}{\left(\frac{1}{2\pi}\right)^2+1}\right]\cos\left(\frac{2\pi x}{L}\right)+\cdots$$
$$= 0.6321206 + 0.1258445\cos\left(\frac{\pi x}{L}\right)$$
$$+0.1115872\cos(2\pi x)+\cdots$$

For purposes of a graph, we let $L = 1$. The following graph shows the function and the third partial sum. It appears that a larger partial sum would be needed for adequate accuracy.



4. Find the one-sided Fourier cosine transform of the function $f(x) = xe^{-ax}$.

$$F(k) = \frac{2}{\sqrt{2\pi}}\int_0^\infty xe^{-ax}\cos(kx)\mathrm{d}x$$
$$= \frac{a^2-k^2}{(a^2+k^2)^2}$$

where have used Eq. (41) of Appendix F.

5. Find the one-sided Fourier sine transform of the function $f(x)=\frac{e^{-ax}}{x}$.

$$F(k)=\frac{2}{\sqrt{2\pi}}\int_0^\infty \frac{e^{-ax}}{x}\sin(kx)$$
$$\mathrm{d}x=\sqrt{\frac{2}{\pi}}\arctan\left(\tfrac{k}{a}\right)$$

where have used Eq. (33) of Appendix F.

6. Find the Fourier transform of the function $\exp[-(x-x_0)^2]$ where a and b are constants.

$$F(k)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\exp[-(x-x_0)^2]e^{-ikx}\mathrm{d}x.$$

Let $u=x-x_0,\ x=u+x_0$

$$\begin{aligned}F(k)&=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}e^{-ik(u+x_0)}\mathrm{d}x\\
&=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\cos[k(u+x_0)]\mathrm{d}x\\
&\quad+\frac{i}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\sin[k(u+x_0)]\mathrm{d}x\\
&=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\cos(ku)\cos(kx_0)\mathrm{d}x\\
&\quad-\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\sin(ku)\sin(kx_0)\mathrm{d}x\\
&\quad+\frac{i}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\sin(ku)\cos(kx_0)\mathrm{d}x\\
&\quad+\frac{i}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\cos(ku)\sin(x_0)\mathrm{d}x\\
&=\frac{\cos(kx_0)}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\cos(ku)\mathrm{d}x\\
&\quad-\frac{\sin(x_0)}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\sin(ku)\mathrm{d}x\\
&\quad+\frac{i\cos(kx_0)}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\sin(ku)\mathrm{d}x\\
&\quad+\frac{i\sin(x_0)}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\cos(ku)\mathrm{d}x\end{aligned}$$

The integrals with $\sin(u)$ vanish since the integrands are odd functions:

$$\begin{aligned}F(k)&=\frac{\cos(kx_0)}{\sqrt{2\pi}}\int_{-\infty}^{\infty}e^{-u^2}\cos(ku)\mathrm{d}x+\frac{i\sin(kx_0)}{\sqrt{2\pi}}\\
&\quad\times\int_{-\infty}^{\infty}e^{-u^2}\cos(ku)\mathrm{d}x\end{aligned}$$

These integrals are the same as for the transform of e^{-x^2}:

$$\begin{aligned}F(k)&=\frac{\cos(kx_0)}{\sqrt{2\pi}}\frac{2}{\sqrt{2\pi}}\frac{1}{2}\sqrt{\pi}e^{-k^2/4}+\frac{i\sin(kx_0)}{\sqrt{2\pi}}\\
&\quad\times\frac{2}{\sqrt{2\pi}}\frac{1}{2}\sqrt{\pi}e^{-k^2/4}\\
&=\frac{1}{2\sqrt{\pi}}[\cos(kx_0)+i\sin(kx_0)]e^{-k^2/4}\\
&=\frac{1}{2\sqrt{\pi}}e^{ikx_0}e^{-k^2/4}\end{aligned}$$

7. Find the one-sided Fourier sine transform of the function ae^{-bx}

$$\begin{aligned}F(k)&=\sqrt{\frac{2}{\pi}}a\int_0^\infty e^{-bx}\sin(kx)\mathrm{d}x\\
&=\sqrt{\frac{2}{\pi}}a\left(\frac{k^2}{b^2+k^2}\right)\end{aligned}$$

where we have used Eq. (26) of Appendix F.

8. Find the one-sided Fourier cosine transform of the function $a/(b^2+t^2)$.

$$\begin{aligned}F(\omega)&=\sqrt{\frac{2}{\pi}}a\int_0^\infty\frac{\cos(\omega t)}{b^2+t^2}\mathrm{d}t=\sqrt{\frac{2}{\pi}}a\frac{\pi}{2b}e^{-a\omega}\\
&=\frac{a}{b}\sqrt{\frac{\pi}{2}}e^{-a\omega}\end{aligned}$$

where we have used Eq. (14) of Appendix F.

9. Find the one-sided Fourier sine transform of the function $f(x)=xe^{-a^2x^2}$.

$$\begin{aligned}F(k)&=\sqrt{\frac{2}{\pi}}\int_0^\infty xe^{-a^2x^2}\sin(kx)\mathrm{d}x\\
&=\sqrt{\frac{2}{\pi}}\frac{m\sqrt{\pi}}{4a^3}e^{-k^2/(4a^2)}=\frac{k\sqrt{2}}{4a^3}e^{-k^2/(4a^2)}\end{aligned}$$

where we have used Eq. (42) of Appendix F.

10. Show that $L\{t\cos(at)\}=(s^2-a^2)/(s^2+a^2)^2$.

$$\int_0^\infty te^{-st}\cos(at)\mathrm{d}t=\frac{s^2-a^2}{(s^2+a^2)^2}$$

where we have used Eq. (41) of Appendix F.

11. Find the Laplace transform of $\cos^2(at)$.

$$\int_0^\infty e^{-st}\cos^2(ax)\mathrm{d}x=\frac{s^2+2a^2}{s(s^2+2a^2)}$$

where we have used Eq. (43) of Appendix F

12. Find the Laplace transform of $\sin^2(at)$.

$$\int_0^\infty e^{-st}\sin^2(ax)\mathrm{d}x=\frac{2a^2}{s(s^2+2a^2)}$$

where we have used Eq. (44) of Appendix F.

13. Use the derivative theorem to derive the Laplace transform of $\cos(at)$ from the Laplace transform of $\sin(at)$.

$$\frac{d\sin(ax)}{\mathrm{d}x} = a\cos(ax)$$

$$\begin{aligned}\mathcal{L}\left\{\frac{\mathrm{d}}{\mathrm{d}t}\sin(at)\right\} &= \mathcal{L}\{a\cos(at)\}\\ &= s\mathcal{L}\{\sin(at)\} - \sin(0)\\ &= \frac{as}{s^2+a^2}\\ \mathcal{L}\{\cos(at)\} &= \frac{s}{s^2+a^2}\end{aligned}$$

14. Find the inverse Laplace transform of $1/(s^2-a^2)$. We recognize this as

$$\frac{1}{s^2-a^2} = \frac{1}{s}\frac{s}{s^2-a^2} = \frac{1}{s}\mathcal{L}\{\cosh(at)\}$$

From the integral theorem

$$\mathcal{L}\left\{\int_0^t \cosh(au)\mathrm{d}u\right\} = \frac{1}{s}\mathcal{L}\{\cosh(at)\}$$

$$\mathcal{L}^{-1}\left\{\frac{s}{s(s^2-a^2)}\right\} = \int_0^t \cosh(ay)\mathrm{d}y$$

$$= \frac{1}{a}\sinh(au)\bigg|_0^t = \frac{1}{a}\sinh(at)$$

in agreement with Table 11.1.

Chapter 12

Differential Equations

EXERCISES

Exercise 12.1. An object falling in a vacuum near the surface of the earth experiences a gravitational force in the z direction given by

$$F_z = -mg$$

where g is called the acceleration due to gravity, and is equal to 9.80 m s^{-2}. This corresponds to a constant acceleration

$$a_z = -g$$

Find the expression for the position of the particle as a function of time. Find the position of the particle at time $t = 1.00$ s if its initial position is $z(0) = 10.00$ m and its initial velocity is $v_z(0) = 0.00$ m s^{-1}

$$\begin{aligned}
v_z(t_1) - v_z(0) &= \int_0^{t_1} a_z(t)\mathrm{d}t = -\int_0^{t_1} g\mathrm{d}t = -gt_1 \\
v_z(t_1) &= -gt_1 \\
z_z(t_2) - z(0) &= \int_0^{t_2} v_z(t_1)\mathrm{d}t_1 = -\int_0^{t_2} gt_1\mathrm{d}t_1 = -\frac{1}{2}gt_2^2 \\
z(t_2) &= z(0) - \frac{1}{2}gt_2^2 \\
z(10.00\text{ s}) &= 10.00\text{ m} - \left(\frac{1}{2}\right)(9.80\text{ m s}^{-2})(1.00\text{ s})^2 \\
&= 10.00\text{ m} - 4.90\text{ m} = 5.10\text{ m}
\end{aligned}$$

Exercise 12.2. Find the general solution to the differential equation

$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2} - 3\frac{\mathrm{d}y}{\mathrm{d}x} + 2y = 0$$

Substitution of the trial solution $y = e^{\lambda x}$ gives the equation

$$\lambda^2 e^{\lambda x} - 3\lambda e^{\lambda x} + 2e^{\lambda x} = 0$$

Division by $e^{\lambda x}$ gives the characteristic equation.

$$\lambda^2 - 3\lambda + 2 = 0$$

This quadratic equation can be factored:

$$(\lambda - 1)(\lambda - 2) = 0$$

The solutions to this equation are

$$\lambda = 1, \quad \lambda = 2.$$

The general solution to the differential equation is

$$y(x) = c_1 e^x + c_2 e^{2x}$$

Exercise 12.3. Show that the function of Eq. (12.21) satisfies Eq. (12.9).

$$\begin{aligned}
z &= b_1 \cos(\omega t) + b_2 \sin(\omega t) \\
\frac{\partial z}{\partial t} &= -\omega b_1 \sin(\omega t) + \omega b_2 \cos(\omega t) \\
\frac{\partial^2 z}{\partial t^2} &= -\omega^2 b_1 \cos(\omega t) - \omega^2 b_2 \sin(\omega t) \\
m\frac{\mathrm{d}^2 z}{\mathrm{d}t^2} &= -\omega^2 m\left[b_1 \cos(\omega t) + b_2 \sin(\omega t)\right] \\
&= -kz
\end{aligned}$$

Exercise 12.4. The frequency of vibration of the H_2 molecule is 1.3194×10^{14} s^{-1}. Find the value of the force constant.

$$\begin{aligned}
\mu N_{Av} &= \frac{(1.0078\text{ g mol}^{-1})^2}{2(1.0078\text{ g mol}^{-1})}\left(\frac{1\text{ kg}}{1000\text{ g}}\right) \\
&= 5.039 \times 10^{-4}\text{ kg mol}^{-1} \\
\mu &= \frac{5.039 \times 10^{-4}\text{ kg mol}^{-1}}{6.02214 \times 10^{23}\text{ mol}^{-1}} = 8.367 \times 10^{-28}\text{ kg} \\
k &= (2\pi\nu)^2\mu = \left[2\pi(1.3194 \times 10^{14}\text{ s}^{-1})\right]^2 \\
&\quad (8.367 \times 10^{-28}\text{ kg}) = 575.1\text{ N m}^{-1}
\end{aligned}$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00036-7

Exercise 12.5. According to quantum mechanics, the energy of a harmonic oscillator is quantized. That is, it can take on only one of a certain set of values, given by

$$E = h\nu\left(\mathrm{v} + \frac{1}{2}\right)$$

where h is Planck's constant, equal to 6.62608×10^{-34}J s, ν is the frequency and v is a quantum number, which can equal $0, 1, 2, \ldots$ The frequency of oscillation of a hydrogen molecule is $1.319 \times 10^{14}\ \mathrm{s}^{-1}$. If a classical harmonic oscillator having this frequency happens to have an energy equal to the $v = 1$ quantum energy, find this energy. What is the maximum value that its kinetic energy can have in this state? What is the maximum value that its potential energy can have? What is the value of the kinetic energy when the potential energy has its maximum value?

$$\begin{aligned} E &= h\nu\left(\tfrac{3}{2}\right) = \tfrac{3}{2}(6.62608\times 10^{-34}\ \mathrm{J\ s})(1.319\times 10^{14}\ \mathrm{s}^{-1}) \\ &= 1.311 \times 10^{-19}\ \mathrm{J} \end{aligned}$$

This is the maximum value of the kinetic energy and also the maximum value of the potential energy. When the potential energy is equal to this value, the kinetic energy vanishes.

Exercise 12.6. Show that $e^{\lambda_1 t}$ does satisfy the differential equation.

$$-\zeta\frac{\mathrm{d}z}{\mathrm{d}t} - kz = m\left(\frac{\mathrm{d}^2 z}{\mathrm{d}t^2}\right)$$

$$-\zeta\lambda_1 e^{\lambda_1 t} - ke^{\lambda_1 t} = m\lambda_1^2 e^{\lambda_1 t}$$

Divide by $e^{\lambda_1 t}$ and substitute the expression for λ_1 into the equation

$$\begin{aligned} &-\zeta\left(-\frac{\zeta}{2m} + \frac{\sqrt{(\zeta/m)^2 - 4k/m}}{2}\right) - k \\ &\quad = m\left(-\frac{\zeta}{2m} + \frac{\sqrt{(\zeta/m)^2 - 4k/m}}{2}\right)^2 \\ &\frac{\zeta^2}{2m} - \frac{\zeta\sqrt{(\zeta/m)^2 - 4k/m}}{2} - k \\ &\quad = m\left[\left(\frac{\zeta}{2m}\right)^2 - \frac{\zeta\sqrt{(\zeta/m)^2 - 4k/m}}{2m}\right. \\ &\qquad \left.+\frac{1}{4}\left((\zeta/m)^2 - 4k/m\right)\right] \\ &\frac{\zeta^2}{2m} - k = m\left(\frac{\zeta}{2m}\right)^2 + \frac{m}{4}\left[(\zeta/m)^2 - 4k/m\right] \\ &\quad = \frac{\zeta^2}{4m} + \frac{\zeta^2}{4m} - k \\ &\quad = \frac{\zeta^2}{2m} - k \end{aligned}$$

Exercise 12.7. If $z(0) = z_0$ and if $v_z(0) = 0$, express the constants b_1 and b_2 in terms of z_0.

$$\begin{aligned} z(t) &= \left[b_1\cos(\omega t) + b_2\sin(\omega t)\right]e^{-\zeta t/2m} \\ z(0) &= b_1 = z_0 \\ v(t) &= \left[b_1\cos(\omega t) + b_2\sin(\omega t)\right]\left(\frac{-\zeta}{2m}\right)e^{-\zeta t/2m} \\ &\quad + \left[-b_1\omega\sin(\omega t) + b_2\omega\cos(\omega t)\right]e^{-\zeta t/2m} \\ v(0) &= b_1\left(\frac{-\zeta}{2m}\right) + b_2\omega = 0 \\ b_2 &= \frac{b_1\zeta}{2m\omega} = \frac{z_0\zeta}{2m\omega} \end{aligned}$$

Exercise 12.8. Substitute this trial solution into Eq. (12.39), using the condition of Eq. (12.40), and show that the equation is satisfied.

The trial solution is

$$z(t) = te^{\lambda t}$$

We substitute the trial solution into this equation and show that it is a valid equation.

$$\begin{aligned} -\zeta\frac{\mathrm{d}z}{\mathrm{d}t} - kz &= m\left(\frac{\mathrm{d}^2 z}{\mathrm{d}t^2}\right) \\ -\zeta\left[e^{\lambda t} + \lambda te^{\lambda t}\right] - kte^{\lambda t} &= m\left[\lambda e^{\lambda t} + \lambda e^{\lambda t} + \lambda^2 te^{\lambda t}\right] \end{aligned}$$

Divide by $me^{\lambda t}$

$$-\frac{\zeta}{m}\left[1 + t\lambda\right] - \frac{k}{m}t = 2\lambda + t\lambda^2$$

Replace k/m by $(\zeta/2m)^2$

$$-\frac{\zeta}{m}[1 + t\lambda] - \left(\frac{\zeta}{2m}\right)^2 t = 2\lambda + t\lambda^2$$

$$-\frac{\zeta}{2m}[2 + 2t\lambda] - \left(\frac{\zeta}{2m}\right)^2 t = 2\lambda + t\lambda^2$$

Let $\zeta/2m = u$

$$\begin{aligned} u^2 t + [2 + 2t\lambda]u + 2\lambda + t\lambda^2 &= 0 \\ t\lambda^2 + (2tu + 2)\lambda + u^2 t + 2u &= 0 \end{aligned}$$

Exercise 12.9. Locate the time at which z attains its maximum value and find the maximum value. The maximum occurs where $\mathrm{d}z/\mathrm{d}t = 0$.

$$c_2 e^{\lambda t} + c_2 t\lambda e^{\lambda t} = 0$$

Divide by $e^{\lambda t}$

$$1.00\ \mathrm{m\ s^{-1}} + (1.00\ \mathrm{m\ s^{-1}})(-1.00\ \mathrm{s^{-1}})t = 0$$

At the maximum

$$t = 1.00 \text{ s}$$

$$z(1.00 \text{ s}) = (1.00 \text{ m s}^{-1})\left[(1.00 \text{ s}^{-1})(t = 1.00 \text{ s})\right] \exp\left[-(1.00 \text{ s}^{-1})(t = 1.00 \text{ s})\right] = (1.00 \text{ m})e^{-1.00} = 0.3679 \text{ m}$$

Exercise 12.10. If $z_c(t)$ is a general solution to the complementary equation and $z_p(t)$ is a particular solution to the inhomogeneous equation, show that z_c+z_p is a solution to the inhomogeneous equation of Eq. (12.1).

Since z_c satisfies the complementary equation

$$f_3(t)\frac{d^3 z_c}{dt^3} + f_2(t)\frac{d^2 z_c}{dt^2} + f_1(t)\frac{dz_c}{dt} = 0$$

Since z_p satisfies the inhomogeneous equation

$$f_3(t)\frac{d^3 z_p}{dt^3} + f_2(t)\frac{d^2 z_p}{dt^2} + f_1(t)\frac{dz_p}{dt} = g(t)$$

Add these two equations

$$f_3(t)\frac{d^3}{dt^3}(z_c+z_p) + f_2(t)\frac{d^2}{dt^2}(z_c+z_p) + f_1(t)\frac{d}{dt}(z_c+z_p) = g(t)$$

Exercise 12.11. Find an expression for the initial velocity.

$$v_z(t) = \frac{dz}{dt} = \frac{d}{dt}\left[b_2\sin(\omega t) + \frac{F_0}{m(\omega^2-\alpha^2)}\sin(\alpha t)\right] = b_2\omega\cos(\omega t) + \frac{F_0\alpha}{m(\omega^2-\alpha^2)}\cos(\alpha t)$$

$$v_z(0) = b_2\omega + \frac{F_0\alpha}{m(\omega^2-\alpha^2)}$$

Exercise 12.12. In a second-order chemical reaction involving one reactant and having no back reaction,

$$-\frac{dc}{dt} = kc^2.$$

Solve this differential equation by separation of variables. Do a definite integration from $t=0$ to $t=t_1$.

$$-\frac{1}{c^2}dc = k\,dt$$

$$-\int_{c(0)}^{c(t_1)}\frac{1}{c^2}dc = \frac{1}{c(t_1)} - \frac{1}{c(t_0)} = k\int_0^{t_1} dt = kt_1$$

$$\frac{1}{c(t_1)} = \frac{1}{c(t_0)} + kt_1$$

Exercise 12.13. Solve the equation $(4x+y)dx + x\,dy = 0$.

Check for exactness

$$\frac{d}{dy}(4x+y) = 1$$

$$\frac{d}{dx}(x) = 1$$

The Pfaffian form is the differential of a function $f = f(x,y)$

$$f(x_1,y_1) - f(x_0,y_0) = \int_{x_0}^{x_1}(4x+y_0)dx + \int_{y_0}^{y_1} x_1\,dy = \left[2x^2 + y_0x\right]\Big|_{x_0}^{x_1} + x_1y|_{y_0}^{y_1}$$

$$2x_1^2 + y_0x_1 - 2x_0^2 - y_0x_0 + x_1y_1 - x_1y_0 = 0$$

$$2x_1^2 - 2x_0^2 - y_0x_0 + x_1y_1 = 0$$

We regard x_0 and y_0 as constants

$$2x_1^2 + x_1y_1 + k = 0$$

We drop the subscripts and solve for y as a function of x.

$$xy = -k - 2x^2$$

$$y = -\frac{k}{x} - 2x$$

This is a solution, but an additional condition would be required to evaluate k. Verify that this is a solution:

$$\frac{dy}{dx} = \frac{k}{x^2} - 2$$

From the original equation

$$\frac{dy}{dx} = -\frac{4x+y}{x} = -4 - \frac{y}{x} = -4 - \left(\frac{1}{x}\right)\left(\frac{k}{x} - 2x\right) = -4 + \frac{k}{x^2} + 2 = \frac{k}{x^2} - 2$$

Exercise 12.14. Show that $1/y^2$ is an integrating factors for the equation in the previous example and show that it leads to the same solution.

After multiplication by $1/y^2$ the Pfaffian form is

$$\frac{1}{y}dx - \frac{x}{y^2}dy = 0$$

This is an exact differential of a function $f = f(x,y)$, since

$$\left[\frac{\partial(1/y)}{\partial y}\right]_x = -\frac{1}{y^2}$$

$$\left[\frac{\partial(-x/y^2)}{\partial x}\right]_y = -\frac{1}{y^2}$$

$$
\begin{aligned}
f(x_1,y_1) - f(x_0,y_0) &= \int_{x_0}^{x_1} \frac{1}{y_0}\mathrm{d}x - \int_{y_0}^{y_1} \frac{x_1}{y^2}\mathrm{d}y = 0 \\
&= \frac{x_1}{y_0} - \frac{x_0}{y_0} + \frac{x_1}{y_1} - \frac{x_1}{y_0} = 0 \\
&= -\frac{y_0}{x_0} + \frac{y_1}{x_1} = 0
\end{aligned}
$$

We regard x_0 and y_0 as constants, so that

$$\frac{y}{x} = \frac{y_0}{x_0} = k$$

where k is a constant. We solve for y in terms of x to obtain the same solution as in the example:

$$y = kx$$

Exercise 12.15. A certain violin string has a mass per unit length of 20.00 mg cm^{-1} and a length of 55.0 cm. Find the tension force necessary to make it produce a fundamental tone of A above middle C (440 oscillations per second = 440 s^{-1} = 440 Hz).

$$\nu = \frac{nc}{2L} = \left(\frac{n}{2L}\right)\left(\frac{T}{\rho}\right)^{1/2}$$

$$
\begin{aligned}
T &= \rho\left(\frac{2L\nu}{n}\right)^2 \\
&= (20.00\ \mathrm{mg\ cm^{-1}})\left(\frac{1\ \mathrm{kg}}{10^6\ \mathrm{mg}}\right)\left(\frac{100\ \mathrm{cm}}{1\ \mathrm{m}}\right) \\
&\quad \left(\frac{2(0.550\ \mathrm{m})(440\ \mathrm{s^{-1}})}{1}\right)^2 = 468.5\ \mathrm{kg\ m\ s^{-2}} \\
&\approx 469\ \mathrm{N}
\end{aligned}
$$

Exercise 12.16. Find the speed of propagation of a traveling wave in an infinite string with the same mass per unit length and the same tension force as the violin string in the previous exercise.

$$
\begin{aligned}
c &= \sqrt{\frac{T}{\rho}} = \left[\left(\frac{469\ \mathrm{N}}{20.00\ \mathrm{mg\ cm^{-1}}}\right)\left(\frac{10^6\ \mathrm{mg}}{1\ \mathrm{kg}}\right)\right]^{1/2} \\
&= 4843\ \mathrm{m\ s^{-1}} \approx 4840\ \mathrm{m\ s^{-1}}
\end{aligned}
$$

Exercise 12.17. Obtain the solution of Eq. (12.1) in the case of critical damping, using Laplace transforms.

The equation is

$$-\zeta\frac{\mathrm{d}z}{\mathrm{d}t} - kz = m\left(\frac{\mathrm{d}^2 z}{\mathrm{d}t^2}\right)$$

with the condition.

$$\left(\frac{\zeta}{2m}\right)^2 = \frac{k}{m}.$$

From the example in Chapter 11 we have the Laplace transform

$$
\begin{aligned}
Z &= \frac{z(0)(s+2a)}{(s+a)^2+\omega^2} + \frac{z^{(1)}(0)}{(s^2+a)^2+\omega^2} \\
&= \frac{z(0)(s+a)}{(s+a)^2+\omega^2} + \frac{az(0)+z^{(1)}(0)}{(s+a)^2+\omega^2}.
\end{aligned}
$$

where

$$a = \frac{\zeta}{2m} \quad \text{and} \quad \omega^2 = \frac{k}{m} - a^2$$

We now apply the critical damping condition

$$a^2 = \frac{k}{m}$$

so that

$$\omega = 0$$

$$Z = \frac{z(0)(s+a)}{(s+a)^2} + \frac{z^{(1)}(0)+az(0)}{(s+a)^2}$$

From Table 11.1 we have

$$
\begin{aligned}
\mathcal{L}^{-1}\left\{\frac{1}{s}\right\} &= 1 \\
\mathcal{L}^{-1}\left\{\frac{1}{s^2}\right\} &= t
\end{aligned}
$$

From the shifting theorem

$$\mathcal{L}\left\{e^{-at}f(t)\right\} = F(s+a)$$

so that

$$z(t) = z(0)e^{-at} + \frac{z^{(1)}(0)+az(0)}{(s+a)^2}te^{-at}$$

Except for the symbols for the constants, this is the same as the solution in the text.

Exercise 12.18. The differential equation for a second-order chemical reaction without back reaction is

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -kc^2,$$

where c is the concentration of the single reactant and k is the rate constant. Set up an Excel spreadsheet to carry out Euler's method for this differential equation. Carry out the calculation for the initial concentration 1.000 mol l^{-1}, k = 1.000 l mol^{-1}s^{-1} for a time of 2.000 s and for Δt = 0.100 s. Compare your result with the correct answer.

Here are the numbers from the spreadsheet

time/s	concentration/mol l^{-1}
0.0	1
0.1	0.9
0.2	0.819
0.3	0.7519239
0.4	0.695384945
0.5	0.647028923
0.6	0.60516428
0.7	0.568541899
0.8	0.53621791
0.9	0.507464946
1.0	0.481712878
1.1	0.458508149
1.2	0.437485176
1.3	0.418345849
1.4	0.400844524
1.5	0.38477689
1.6	0.369971565
1.7	0.356283669
1.8	0.343589864
1.9	0.331784464
2.0	0.320776371

The result of the spreadsheet calculation is

$$c(t) \approx 0.3208 \text{ mol l}^{-1}$$

Solving the differential equation by separation of variables:

$$\frac{\mathrm{d}c}{c^2} = -k\,\mathrm{d}t$$
$$-\left.\frac{1}{c}\right|_{c(0)}^{c(t)} = -\frac{1}{c(t)} + \frac{1}{c(t)} = -kt$$

$$\frac{1}{c(t)} = \frac{1}{1.000 \text{ mol l}^{-1}} + \left(1.000 \text{ l mol}^{-1}\text{ s}^{-1}\right)(2.000 \text{ s})$$
$$= 3.000 \text{ l mol}^{-1}$$
$$c(t) = 0.3333 \text{ mol l}^{-1}$$

PROBLEMS

1. An object moves through a fluid in the x direction. The only force acting on the object is a frictional force that is proportional to the negative of the velocity:

$$F_x = -\zeta v_x = -\zeta\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right).$$

Write the equation of motion of the object. Find the general solution to this equation, and obtain the particular solution that applies if $x(0) = 0$ and $v_x(0) = v_0 =$ constant. Construct a graph of the position as a function of time. The equation of motion is

$$\left(\frac{\mathrm{d}^2x}{\mathrm{d}t^2}\right) = -\frac{\zeta}{m}\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)$$

The trial solution is

$$x = e^{\lambda t}$$

$$\lambda^2 e^{\lambda t} = -\frac{\zeta}{m}\lambda e^{\lambda t}$$

The characteristic equation is

$$\lambda^2 + \frac{\zeta}{m}\lambda = 0$$

The solution is

$$\lambda = \begin{cases} 0 \\ -\frac{\zeta}{m} \end{cases}$$

The general solution is

$$x = c_1 + c_2 \exp\left(-\frac{\zeta t}{m}\right)$$

The velocity is

$$v = -c_2\left(\frac{\zeta}{m}\right)\exp\left(-\frac{\zeta t}{m}\right)$$

$$v_0 = -c_2\left(\frac{\zeta}{m}\right)$$
$$c_2 = -\frac{mv_0}{\zeta}$$

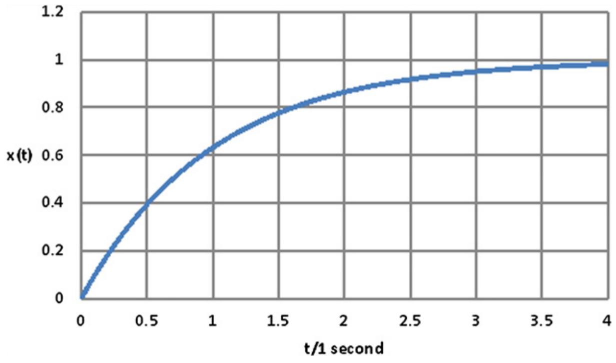
The initial position is

$$x(0) = 0 = c_1 + c_2$$
$$c_1 = \frac{mv_0}{\zeta}$$

The particular solution is

$$x = \frac{mv_0}{\zeta}\left[1 - \exp\left(-\frac{\zeta t}{m}\right)\right]$$

For the graph, we let $mv_0/\zeta = 1, \zeta/m = 1$.



2. A particle moves along the z axis. It is acted upon by a constant gravitational force equal to $-$kmg , where k is the unit vector in the z direction. It is also acted on by a frictional force given by

$$\mathbf{F}_f = -\mathbf{k}\zeta\left(\frac{dz}{dt}\right).$$

where ζ is a constant called a "friction constant." Find the equation of motion and obtain a general solution. Find the particular solution for the case that $z(0) = 0$ and $v_x(0) = 0$. Construct a graph of z as a function of time for this case. The equation of motion is

$$\frac{d^2z}{dt^2} + \frac{\zeta}{m}\left(\frac{dz}{dt}\right) = -g$$

$$\frac{d^2z}{dt^2} + a\left(\frac{dz}{dt}\right) + b = 0$$

where

$$a = \frac{\zeta}{m}; b = g$$

This is a linear inhomogeneous equation. The complementary equation is

$$\frac{d^2z}{dt^2} + \frac{\zeta}{m}\left(\frac{dz}{dt}\right) = 0$$

The trial solution to the complementary equation is

$$z = e^{\lambda t}$$

The characteristic equation is

$$\lambda^2 + \frac{\zeta}{m}\lambda = 0$$

This equation has the solution

$$\lambda = \begin{cases} 0 \\ -\frac{\zeta}{m} \end{cases}$$

The solution to the complementary equation is

$$z = c_1 + c_2 \exp\left(-\frac{\zeta t}{m}\right)$$

To find a particular solution, we apply the variation of parameters method. From Table 12.1, the recommended trial solution for a constant inhomogeneous term is a constant, A.

$$\frac{d^2A}{dt^2} + \frac{\zeta}{m}\left(\frac{dA}{dt}\right) = -g$$

This won't work, since the left-hand side of the equation vanishes. We try the next trial solution

$$z = A_0 + A_1 t$$

substitution into the inhomogeneous equation gives

$$\begin{aligned} 0 + \frac{\zeta}{m}A_1 &= -g \\ A_1 &= -\frac{mg}{\zeta} \end{aligned}$$

Our solution is now

$$z = A_0 + c_1 - \frac{mgt}{\zeta} + c_2 \exp\left(-\frac{\zeta t}{m}\right)$$

$$\left(\frac{m}{\zeta}\right)^2 g - \frac{C_4 m}{\zeta} - \left(\frac{m}{\zeta}\right) gt + C_5 e^{-\zeta t/m}$$

The velocity is

$$v = -\frac{mg}{\zeta} - c_2\left(\frac{\zeta}{m}\right)\exp\left(-\frac{\zeta t}{m}\right)$$

where the constants would be evaluated to suit a specific case. We consider the case that $z(0) = 0, v(0) = 0$. From the velocity condition

$$v(0) = -\frac{mg}{\zeta} - c_2\left(\frac{\zeta}{m}\right) = 0$$

$$c_2 = \left(\frac{m}{\zeta}\right)^2 g$$

$$z = A_0 + c_1 - \frac{mgt}{\zeta} + \left(\frac{m}{\zeta}\right)^2 g \exp\left(-\frac{\zeta t}{m}\right)$$

From the position condition

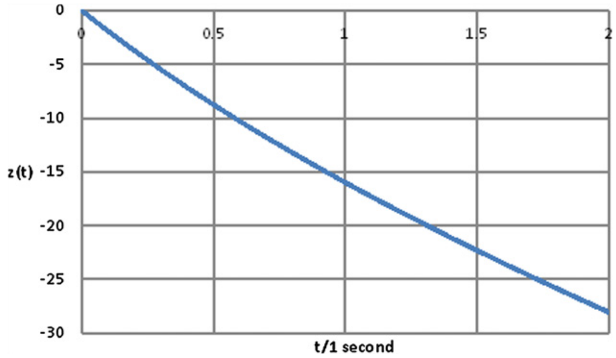
$$z(0) = A_0 + c_1 + \left(\frac{m}{\zeta}\right)^2 g = 0$$

$$A_0 + c_1 = -\left(\frac{m}{\zeta}\right)^2 g$$

For our case,

$$\begin{aligned} z &= -\left(\frac{m}{\zeta}\right)^2 g - \frac{mgt}{\zeta} + \left(\frac{m}{\zeta}\right)^2 g \exp\left(-\frac{\zeta t}{m}\right) \\ &= -\frac{mgt}{\zeta} + \left(\frac{m}{\zeta}\right)^2 g\left[\exp\left(-\frac{\zeta t}{m}\right) - 1\right] \end{aligned}$$

We construct a graph, assuming for convenience that $m/\zeta = 1$.



Notice that the graph is nearly linear toward the end of the graph, when the particle would have nearly reached its terminal velocity.

3. An object sliding on a solid surface experiences a frictional force that is constant and in the opposite direction to the velocity if the particle is moving, and is zero it is not moving. Find the position of the particle as a function of time if it moves only in the x direction and the initial position is $x(0) = 0$ and the initial velocity is $v_x(0) = v_0 =$ constant. Proceed as though the constant force were present at all times and then cut the solution off at the point at which the velocity vanishes. That is, just say that the particle is fixed after this time. Construct a graph of x as a function of time for the case that $v_0 = 10.00$ m s^{-1}. The equation of motion is

$$\frac{d^2x}{dt^2} = -\frac{F_0}{m}$$

Except for the symbols used, this is the same as the equation of motion for a free-falling object. The solution is

$$\begin{aligned}
v(t_1) - v(0) &= \textstyle\int_0^{t_1} a_z(t)dt = -\int_0^{t_1}\left(\frac{F_0}{m}\right)dt \\
&= -\left(\tfrac{F_0}{m}\right)t_1 \\
x(t_2) - x(0) &= \int_0^{t_2} v(t_1)dt_1 \\
&= \int_0^{t_2}\left(v(0) - \left(\frac{F_0}{m}\right)t_1\right)dt_1 \\
&= v(0)t_2 - \int_0^{t_2}\left(\frac{F_0}{m}\right)t_1 dt_1 \\
&= v(0)t_2 - \frac{1}{2}\left(\frac{F_0}{m}\right)t_2^2
\end{aligned}$$

For the case that $x(0) = 0$,

$$x(t) = -\frac{1}{2}\left(\frac{F_0}{m}\right)t^2$$

The time at which the velocity vanishes is given by

$$0 = v_0 - \left(\frac{F_0}{m}\right)t_{stop}$$

$$t_{stop} = \frac{mv_0}{F_0}$$

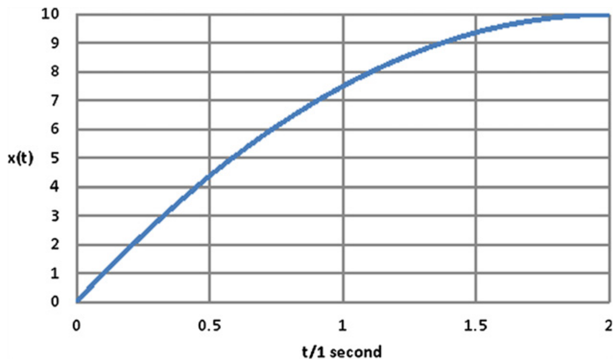
For a graph, we assume that

$$v_o = 10.00 \text{ m s}^{-1};\ m = 1.000 \text{ kg};\ F_0 = 5.00 \text{ N}$$

$$t_{stop} = \frac{mv_0}{F_0} = \frac{(1.000 \text{ kg})\left(10.00 \text{ m s}^{-1}\right)}{5.00 \text{ kg m s}^{-2}} = 2.00 \text{ s}$$

For this case

$$\begin{aligned}
x &= (10.00 \text{ m s}^{-1})t - \tfrac{1}{2}\left(\tfrac{5.00 \text{ kg m s}^{-2}}{1.000 \text{ kg}}\right) \\
t^2 &= \left(10.00 \text{ m s}^{-1}\right)t - (2.500 \text{ m s}^{-2})t^2
\end{aligned}$$



4. A harmonic oscillator has a mass $m = 0.300$ kg and a force constant $k = 155$ N m^{-1}.

a. Find the period and the frequency of oscillation.

$$\tau = 2\pi\sqrt{\frac{m}{k}} = 2\pi\left(\frac{0.300 \text{ kg}}{155 \text{ N m}^{-1}}\right)^{1/2} = 0.276 \text{ s}$$

$$\nu = \frac{1}{\tau} = \frac{1}{0.276 \text{ s}} = 3.62 \text{ s}^{-1}$$

b. Find the value of the friction constant ζ necessary to produce critical damping with this oscillator. Find the value of the constant λ. For critical damping

$$\left(\frac{\zeta}{2m}\right)^2 = \frac{k}{m}$$

$$\begin{aligned}
\zeta &= 2m\sqrt{\frac{k}{m}} = 2\sqrt{km} \\
&= 2\left[\left(155 \text{ N m}^{-1}\right)\left(0.300 \text{ kg}\right)\right]^{1/2} \\
&= 13.6 \text{ kg s}^{-1}
\end{aligned}$$

For critical damping

$$\lambda = -\frac{\zeta}{2m} = -\frac{13.6 \text{ kg s}^{-1}}{2\left(0.300 \text{ kg}\right)} = -22.7 \text{ s}^{-1}$$

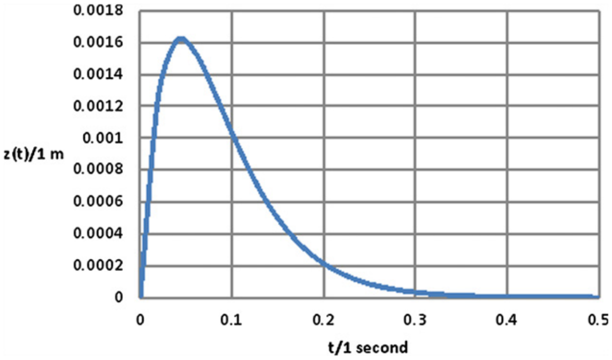
c. Construct a graph of the position of the oscillator as a function of t for the initial conditions $z(0) = 0, v_z(0) = 0.100 \text{ m s}^{-1}$.

$$z(t) = (c_1 + c_2 t)e^{\lambda t}$$

For these conditions

$$c_1 = 0$$

$$v = c_2 e^{\lambda t} + c_2 t\lambda e^{\lambda t} = c_2(1 + t\lambda)e^{\lambda t}$$
$$v(0) = c_2 = 0.100 \text{ m s}^{-1}$$
$$z = (0.100 \text{ m s}^{-1})(t)\exp[-(22.7 \text{ s}^{-1})t]$$



5. A less than critically damped harmonic oscillator has a mass $m = 0.3000$ kg, a force constant $k = 98.00 \text{ N m}^{-1}$ and a friction constant $\zeta = 1.000 \text{ kg s}^{-1}$.

a. Find the circular frequency of oscillation ω and compare it with the frequency that would occur if there were no damping.

$$\omega = \sqrt{\frac{k}{m} - \left(\frac{\zeta}{2m}\right)^2}$$
$$= \left[\frac{98.00 \text{ N m}^{-1}}{0.3000 \text{ kg}} - \left(\frac{1.000 \text{ kg s}^{-1}}{2\left(0.3000 \text{ kg}\right)}\right)^2\right]^{1/2}$$
$$= 18.00 \text{ s}^{-1}$$

Without damping

$$\omega = \sqrt{\frac{k}{m}} = \left[\frac{98.00 \text{ N m}^{-1}}{0.3000 \text{ kg}}\right]^{1/2} = 18.07 \text{ s}^{-1}$$

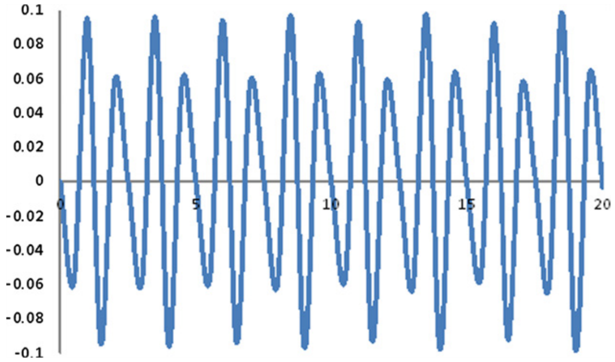
b. Find the time required for the real exponential factor in the solution to drop to one-half of its value at $t = 0$.

$$e^{-\zeta t/2m} = \frac{1}{2}$$
$$\frac{\zeta t}{2m} = -\ln(0.5000) = \ln(2.000)$$
$$t = \frac{2m\ln(2.000)}{\zeta}$$
$$= \frac{2\left(0.300 \text{ kg}\right)\ln(2.000)}{1.000 \text{ kg s}^{-1}} = 0.4159 \text{ s}$$

6. A forced harmonic oscillator with a circular frequency $\omega = 6.283 \text{ s}^{-1}$ (frequency $\nu = 1.000 \text{ s}^{-1}$ is exposed to an external force $F_0 \sin(\alpha t)$ with circular frequency $\alpha = 7.540 \text{ s}^{-1}$ such that in the solution of Eq. (12.5) becomes

$$z(t) = \sin(\omega t) + 0.100\sin(\alpha t)$$
$$= \sin\left[(6.283 \text{ s}^{-1})t\right]$$
$$+ (0.100)\sin\left[(7.540 \text{ s}^{-1})t\right]$$

Using Excel or Mathematica, make a graph of $z(t)$ for a time period of at least 20 s . Here is a graph constructed with Excel:



7. A forced harmonic oscillator with mass $m = 0.200$ kg and a circular frequency $\omega = 6.283 \text{ s}^{-1}$ (frequency $\nu = 1.000 \text{ s}^{-1}$) is exposed to an external force $F_0\exp(-\alpha t)$ with $\alpha = 0.7540 \text{ s}^{-1}$. Find the solution to its equation of motion. Construct a graph of the motion for several values of F_0. The solution to the complementary equation is

$$z_c = b_1\cos(\omega t) + b_2\sin(\omega t)$$

Table 12.1 gives the trial particular solution

$$z_p = Ae^{-\alpha t}$$

We need to substitute this into the differential equation

$$\frac{d^2z}{dt^2} + \frac{k}{m}z = \frac{d^2z}{dt^2} + \omega^2 z = \frac{F_0\exp(-\alpha t)}{m}$$

$$A\alpha^2 e^{-\alpha t} + \omega^2 A e^{-\alpha t} = \frac{F_0 e^{-\alpha t}}{m}$$

Divide by $e^{-\alpha t}$.

$$A\alpha^2 + \omega^2 A = \frac{F_0}{m}$$

Solve for A

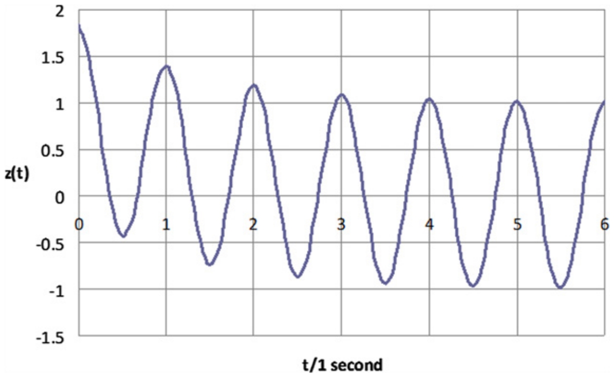
$$A = \frac{F_0}{m(a^2 + \omega^2)}$$

The solution to the differential equation is

$$z = b_1 \cos(\omega t) + b_2 \sin(\omega t) + \frac{F_0 e^{-\alpha t}}{m(a^2 + \omega^2)}$$

For our first graph, we take the case that $b_1 = 1.000$ m, $b_2 = 0$, and $F_0 = 10.000$ N

$$\begin{aligned} z &= \cos\left[(6.283)t\right] \\ &\quad + \frac{(10.000\ \mathrm{N})\exp\left[(0.7540\ \mathrm{s}^{-1})t\right]}{(0.300\ \mathrm{kg})\left[(0.7540\ \mathrm{s}^{-1})^2 + (6.283\ \mathrm{s}^{-1})^2\right]} \\ &= \cos[(6.283)t] + 0.8324\exp[-(0.7540)t] \end{aligned}$$



Other graphs will be similar.

8. A tank contains a solution that is rapidly stirred, so that it remains uniform at all times. A solution of the same solute is flowing into the tank at a fixed rate of flow, and an overflow pipe allows solution from the tank to flow out at the same rate. If the solution flowing in has a fixed concentration that is different from the initial concentration in the tank, write and solve the differential equation that governs the number of moles of solute in the tank. The inlet pipe allows A moles per hour to flow in and the overflow pipe allows Bn moles per hour to flow out, where A and B are constants and n is the number of moles of solute in the tank. Find the values of A and B that correspond to a volume in the tank of 100.0 l, an input of 1.000 l h^{-1} of a solution with 1.000 mol l^{-1}, and an output of 1.000 l h^{-1} of the solution in the tank. Find the concentration in the tank after 4.00 h, if the initial concentration is zero.

$$\frac{dn}{dt} = A - Bn$$

This is an inhomogeneous equation. The complementary equation is

$$\frac{dn_c}{dt} + Bn_c = 0$$

$$n_c = Ce^{-Bt}$$

where C is a constant. The particular solution from Table 12.1 is

$$n_p = K$$

where K is a constant.

$$\begin{aligned} \frac{dK}{dt} &= 0 = A - BK \\ K &= \frac{A}{B} \end{aligned}$$

The general solution is

$$n = Ce^{-Bt} + \frac{A}{B}$$

At $t = 0$, $n = 0$

$$C = -\frac{A}{B}$$

$$n(t) = \frac{A}{B}(1 - e^{-Bt})$$

The molar concentration is

$$c = \frac{n}{100.0\ \mathrm{l}}$$

$$\begin{aligned} Bn &= (1.000\ \mathrm{l\ h^{-1}})c = \frac{1.000\ \mathrm{l\ h^{-1}}}{100.0\ \mathrm{l}} n \\ &= (0.0100\ \mathrm{h^{-1}})n \\ B &= 0.0100\ \mathrm{h^{-1}} \\ A &= 1.000\ \mathrm{mol\ h^{-1}} \end{aligned}$$

$$\begin{aligned} n(t) &= \frac{A}{B}(1 - e^{-Bt}) = \frac{1.000\ \mathrm{mol\ h^{-1}}}{0.0100\ \mathrm{h^{-1}}} \\ &\quad \left[1 - \exp(-0.0100\ \mathrm{h^{-1}}t)\right] \\ &= (100.0\ \mathrm{mol})\left[1 - \exp(-0.0100\ \mathrm{h^{-1}}t)\right] \end{aligned}$$

At $t = 4.00$ h

$$\begin{aligned} n(4.00\ \mathrm{h}) &= (100.0\ \mathrm{mol})\left[1 - \exp(-0.0400)\right] \\ &= 3.92\ \mathrm{mol} \end{aligned}$$

9. An nth-order chemical reaction with one reactant obeys the differential equation

$$\frac{dc}{dt} = -kc^n$$

where c is the concentration of the reactant and k is a constant. Solve this differential equation by separation of variables. If the initial concentration is c_0 moles per liter, find an expression for the time required for half of the reactant to react.

$$\int_{c(0)}^{c(t_1)} \frac{1}{c^n}\mathrm{d}c = -k\int_0^{t_1}\mathrm{d}t$$

$$-\frac{1}{n-1}\left.\frac{1}{c^{n-1}}\right|_{c(0)}^{c(t_1)} = -kt_1$$

$$\frac{1}{(n-1)\,c(t_1)^{n+1}} - \frac{1}{(n-1)\,c(0)^{n+1}} = kt$$

$$\frac{1}{c(t_1)^{n-1}} = \frac{1}{c(0)^{n-1}} + (n-1)kt$$

For half of the original amount to react

$$\frac{2^{n-1}}{c(0)^{n-1}} - \frac{1}{c(0)^{n-1}} = (n-1)kt_{1/2}$$

$$\frac{2^{n-1}-1}{c(0)^{n-1}} = (n-1)kt_{1/2}$$

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)kc(0)^{n+1}}$$

10. Find the solution to the differential equation

$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2} - \frac{\mathrm{d}y}{\mathrm{d}x} - 2y = e^x$$

This is an inhomogeneous equation. The complementary equation is

$$\frac{\mathrm{d}^2y_c}{\mathrm{d}x^2} - \frac{\mathrm{d}y_c}{\mathrm{d}x} - 2y_c = 0$$

With the trial solution $y = e^{\lambda x}$. The characteristic equation for this differential equation is

$$\lambda^2 - \lambda - 2 = 0 = (x-2)(x+1)$$

This has the solution

$$\lambda = \begin{cases} 2 \\ -1 \end{cases}$$

$$y_c = c_1e^{2x} - c_2e^{-x}$$

From Table 12.1, a particular solution is

$$y_p = Ae^{\alpha x}$$

$$\frac{\mathrm{d}y_p}{\mathrm{d}x} = aAe^{\alpha x}$$

$$\frac{\mathrm{d}^2y_p}{\mathrm{d}x^2} = a^2Ae^{\alpha x}$$

$$\frac{\mathrm{d}^2y_c}{\mathrm{d}x^2} - \frac{\mathrm{d}y_c}{\mathrm{d}x} - 2y_c = a^2Ae^{\alpha x} - aAe^{\alpha x} - 2Ae^{\alpha x} = e^x$$

Divide by e^{ax}

$$A(a^2 - a - 2) = e^{x-ax}$$

$$A = \frac{e^{x(1-a)}}{a^2-a-2}$$

this can be a correct equation only if $a - 1$.

$$A = -\frac{1}{2}$$

The solution is

$$y = c_1e^{2x} - c_2e^{-x} - \frac{1}{2}e^x$$

11. Test the following equations for exactness, and solve the exact equations:

a. $(x^2 + xy + y^2)\mathrm{d}x + (4x^2 - 2xy + 3y^2)\mathrm{d}y = 0$

$$\frac{\mathrm{d}}{\mathrm{d}y}(x^2 + xy + y^2) = x + 2y$$

$$\frac{\mathrm{d}}{\mathrm{d}x}(4x^2 - 2xy + 3y^2) = 8x - y$$

Not exact

b.

$$ye^x\mathrm{d}x + e^x\mathrm{d}y = 0$$

$$\frac{\mathrm{d}}{\mathrm{d}y}ye^x = e^x$$

$$\frac{\mathrm{d}}{\mathrm{d}x}e^x = e^x$$

This is exact. the Pfaffian form is the differential of a function, $f = f(x,y)$. Do a line integral as in the example

$$\int_c \mathrm{d}f = 0 = \int_{x_1}^{x_2} y_1e^x\mathrm{d}x + \int_{y_1}^{y_2} e^{x_2}\mathrm{d}y$$

$$= y_1(e^{x_2} - e^{x_1}) + e^{x_2}(y_2 - y_1) = 0$$

$$= y_1(-e^{x_1}) + e^{x_2}(y_2)$$

We regard x_1 and y_1 as constants, and drop the subscripts on x_2 and y_2

$$ye^x = C$$

$$y = Ce^x$$

where C is a constant

c.

$$[2xy - \cos(x)]\mathrm{d}x + (x^2 - 1)\mathrm{d}y = 0$$

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \frac{2xy - \cos(x)}{x^2-1}$$

$$\frac{d}{dy}[2xy - \cos(x)] = 2x$$
$$\frac{d}{dy}(x^2 - 1) = 2x$$

This is exact. the Pfaffian form is the differential of a function, $f = f(x,y)$. Do a line integral as in the example

$$\int_c df = 0 = \int_{x_1}^{x_2} [2xy_1 - \cos(x)]dx + \int_{y_1}^{y_2} (x_2^2 - 1)dy$$
$$= y_1(x_2^2 - x_1^2) - \sin(x_2) + \sin(x_1) + (x_2^2 - 1)(y_2 - y_1)$$
$$= y_1(-x_1^2) - \sin(x_2) + \sin(x_1) + (x_2^2 - 1)(y_2)$$

We regard $x_1$and $y_1$as constants, and drop the subscripts on x_2 and y_2

$$y(x^2 - 1) - \sin(x) = C$$

where C is a constant.

$$y = \frac{C + \sin(x)}{x^2 - 1}$$

12. Use Mathematica to solve the differential equation symbolically

$$\frac{dy}{dx} + y\cos(x) - e^{-\sin(x)} = 0$$

The solution is

$$y = Ce^{-\sin(x)} + \frac{x}{e^{\sin(x)}}$$

where C is constant.

13. Use Mathematica to obtain a numerical solution to the differential equation in the previous problem for the range $0 < x < 10$ and for the initial condition $y(0) = 1$. Evaluate the interpolating function for several values of x and make a plot of the interpolating function for the range $0 < x < 10$.

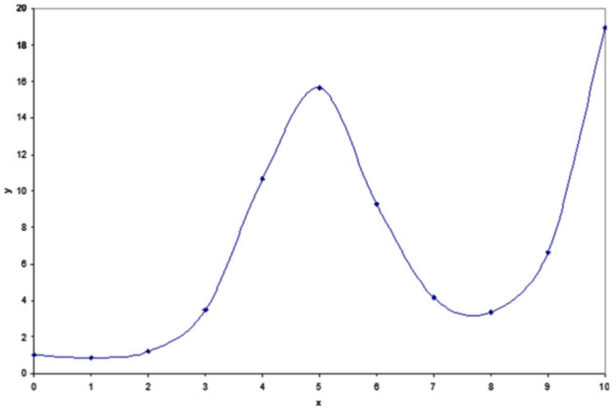
$$\frac{dy}{dx} + y\cos(x) = e^{-\sin(x)}$$

$$\frac{dy}{dx} + y\cos(x) = e^{-\sin(x)}$$
$$y(0) = 1$$

Here are the values for integer values of x from $x = 0$ to $x = 10$

$$\begin{bmatrix} 1.0 \\ 0.86215 \\ 1.2084 \\ 3.4735 \\ 10.657 \\ 15.653 \\ 9.2565 \\ 4.1473 \\ 3.3463 \\ 6.6225 \\ 18.952 \end{bmatrix}$$

Here is a graph of the values



14. Solve the differential equation:

$$\frac{d^2y}{dx^2} - 4y = 2e^{3x} + \sin(x)$$

This is an inhomogeneous equation and the complementary equation is

$$\frac{d^2y_c}{dx^2} - 4y_c = 0$$

Take the trial solution of the complementary equation:

$$y_c = e^{\lambda x}$$

$$\lambda^2 e^{\lambda x} - 4e^{\lambda x} = 0$$
$$\lambda^2 - 4 = 0$$
$$\lambda = \pm 2$$

The solution of the complementary equation is

$$y_c = c_1 e^{2x} + c_2 e^{-2x}$$

To seek a particular solution, since we have two terms in the inhomogeneous term, we try

$$\begin{aligned} y_p &= Ae^{ax} + B\cos(x) + C\sin(x) \\ \frac{d^2y_p}{dx^2} &= \frac{dy}{dx}\left[Aae^{ax} - B\sin(x) + C\cos(x)\right] \\ &= Aa^2e^{ax} - B\cos(x) - C\sin(x) \end{aligned}$$

$$\begin{aligned} &Aa^2e^{ax} - B\cos(x) - C\sin(x) - 4 \\ &\left[Ae^{ax} + \left[B\cos(x) + C\sin(x)\right]\right] = 2e^{3x} + \sin(x) \\ &-5Aa^2e^{ax} - 5B\cos(x) - 5C\sin(x) = 2e^{3x} + \sin(x) \end{aligned}$$

This be a valid equation only if $a = 3$ and $B = 0$

$$\begin{aligned} 9Ae^{3x} &- 4Ae^{3x} - C\sin(x) - 4C\sin(x) \\ &= 2e^{3x} + \sin(x) \\ 5Ae^{3x} &- 5C\sin(x) = 2e^{3x} + \sin(x) \\ A &= \frac{2}{5} \\ C &= -\frac{1}{5} \end{aligned}$$

The solution is

$$\begin{aligned} y &= c_1e^{2x} + c_2e^{-2x} + \frac{2}{5}e^{3x} - \frac{1}{5}\sin x \\ &= c_1e^{2x} + c_2e^{-2x} + \frac{2}{5}e^{3x} - \frac{1}{5}\sin x \end{aligned}$$

15. Radioactive nuclei decay according to the same differential equation that governs first-order chemical reactions. In living matter, the isotope ^{14}C is continually replaced as it decays, but it decays without replacement beginning with the death of the organism. The half-life of the isotope (the time required for half of an initial sample to decay) is 5730 years. If a sample of charcoal from an archaeological specimen exhibits 1.27 disintegrations of ^{14}C per gram of carbon per minute and wood recently taken from a living tree exhibits 15.3 disintegrations of ^{14}C per gram of carbon per minute, estimate the age of the charcoal.

$$\begin{aligned} N(t) &= N(0)e^{-kt} \\ \frac{1}{2} &= e^{-kt_{1/2}} \\ -kt_{1/2} &= \ln(1/2 = -\ln(2) \\ k &= \frac{\ln(2)}{t_{1/2}} = \frac{\ln(2)}{5739\text{ y}} = 1.210\times10^{-4}\text{ y}^{-1} \end{aligned}$$

The rate of disintegrations is proportional to the number of atoms present:

$$\begin{aligned} \frac{N(t)}{N(0)} &= \frac{1.27}{15.3} = 0.0830 = e^{-kt} \\ -kt &= \ln(0.0830) \\ t &= \frac{-\ln(0.0830)}{1.210\times10^{-4}\text{ y}^{-1}} = 2.06\times10^{4}\text{y} \\ &= 20600\text{ y} \end{aligned}$$

16. A pendulum of length L oscillates in a vertical plane. Assuming that the mass of the pendulum is all concentrated at the end of the pendulum, show that it obeys the differential equation

$$L\left(\frac{d^2\phi}{dt^2}\right) = -g\sin(\phi)$$

where g is the acceleration due to gravity and ϕ is the angle between the pendulum and the vertical. This equation cannot be solved exactly. For small oscillations such that

$$\sin(\phi) \approx \phi$$

find the solution to the equation. What is the period of the motion? What is the frequency? Find the value of L such that the period equals 2.000 s.

$$\frac{d^2\phi}{dt^2} = -\frac{g}{L}\phi$$

The real solution to this equation is

$$\phi = c_1\sin\left(\sqrt{\frac{g}{L}}t\right) + c_2\sin\left(\sqrt{\frac{g}{L}}t\right)$$

The circular frequency is

$$\omega = \sqrt{\frac{g}{L}}$$

and the frequency is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{g}{L}}$$

The period is

$$\tau = \frac{1}{\nu} = 2\pi\sqrt{\frac{L}{g}}$$

To have a period of 2.000 s

$$\begin{aligned} L &= g\left(\frac{\tau}{2\pi}\right)^2 = (9.80\text{ m s}^{-2})\left(\frac{2.000\text{ s}}{2\pi}\right)^2 \\ &= 0.9930\text{ m} \end{aligned}$$

17. Use Mathematica to obtain a numerical solution to the pendulum equation in the previous problem without approximation for the case that $L = 1.000$ m with the initial conditions $\phi(0) = 0.350$ rad (about 20°) and $d\phi/dt = 0$. Evaluate the solution for $t = 0.500$ s, 1.000 s, and 1.500 s. Make a graph of your solution for $0 < t < 4.00$ s. Repeat your solution for $\phi(0) = 0.050$ rad (about 2.9°) and $d\phi/dt = 0$. Determine the period and the frequency from your graphs.

How do they compare with the solution from the previous problem?

$$L\left(\frac{d^2\phi}{dt^2}\right) = -g\sin(\phi)$$

$$\frac{d^2\phi}{dt^2} = -9.80\sin(\phi)$$

$$\phi(0) = 0.350$$

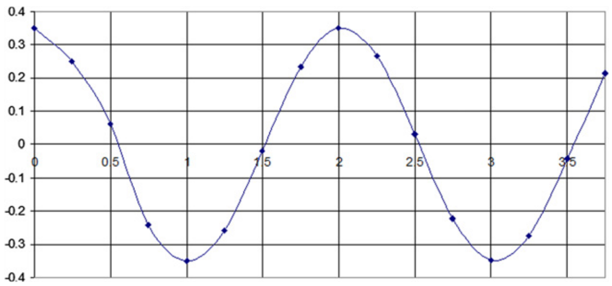
$$\phi'' = -9.80\sin(\phi)$$

$$\phi'(0) = 0$$

$$\phi(0) = 0.350$$

$$\phi\begin{bmatrix} 0.5 \\ 1 \\ 1.5 \end{bmatrix} = \begin{bmatrix} 6.1493\times 10^{-3} \\ -0.34979 \\ -0.01844 \end{bmatrix}$$

$$\phi\begin{bmatrix} 0 \\ 0.25 \\ 0.5 \\ 0.75 \\ 1 \\ 1.25 \\ 1.5 \\ 1.75 \\ 2 \\ 2.25 \\ 2.5 \\ 2.75 \\ 3 \\ 3.25 \\ 3.5 \\ 3.75 \end{bmatrix} = \begin{bmatrix} 0.35 \\ 0.24996 \\ 6.1493\times 10^{-3} \\ -0.24122 \\ -0.34979 \\ -0.25839 \\ -0.01844 \\ 0.23219 \\ 0.34914 \\ 0.2665 \\ 3.0708\times 10^{-2} \\ -0.22286 \\ -0.34808 \\ -0.27429 \\ -4.2938\times 10^{-2} \\ 0.21326 \end{bmatrix}$$



From the graph, the period appears to be about 2.1 s. From the method of the pervious problem

$$\tau = 2\pi\sqrt{\frac{L}{g}} = 2\pi\left(\frac{1.000 \text{ m}}{9.80 \text{ m s}^{-2}}\right)^{1/2} = 2.007 \text{ s}$$

For the second case

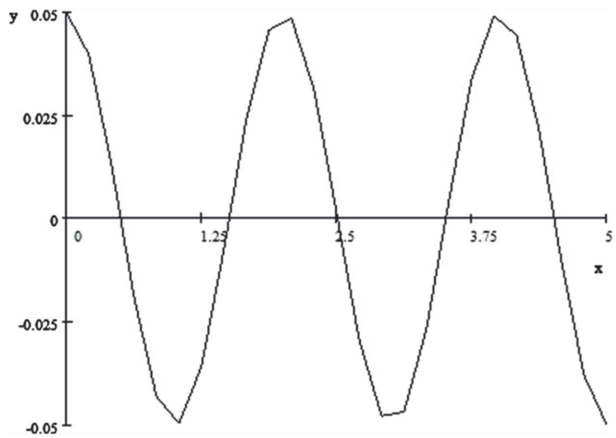
$$\phi'' = -9.80\sin(\phi)$$

$$\phi'(0) = 0$$

$$\phi(0) = 0.050$$

Here are the values for plotting:

$$\phi\begin{bmatrix} 0 \\ 0.25 \\ 0.5 \\ 0.75 \\ 1.00 \\ 1.25 \\ 1.50 \\ 1.5 \\ 1.75 \\ 2.00 \\ 2.25 \\ 2.50 \\ 2.75 \\ 3.00 \\ 3.25 \\ 3.5 \end{bmatrix} = \begin{bmatrix} 0.05 \\ 3.5459\times 10^{-2} \\ 2.8968\times 10^{-4} \\ -3.5048\times 10^{-2} \\ -4.9997\times 10^{-2} \\ -3.5865\times 10^{-2} \\ -8.6900\times 10^{-4} \\ -8.6900\times 10^{-4} \\ 3.4632\times 10^{-2} \\ 4.9987\times 10^{-2} \\ 3.6266\times 10^{-2} \\ 1.4482\times 10^{-3} \\ -3.4212\times 10^{-2} \\ -4.9970\times 10^{-2} \\ -3.6662\times 10^{-2} \\ -2.0272\times 10^{-3} \end{bmatrix}$$



The period appears again to be near 2.1 s.

18. Obtain the solution for Eq. (12.4) for the forced harmonic oscillator using Laplace transforms.

$$\frac{d^2z}{dt^2} + \frac{k}{m}z = \frac{d^2z}{dt^2} + \omega^2 z = \frac{F_0\sin(\alpha t)}{m}$$

$$s^2Z - sz(0) - z^{(1)}(0) + \omega^2 Z = \frac{F_0}{m}\frac{\alpha}{s^2+\alpha^2}$$

$$Z(s^2+\omega^2) = \frac{F_0}{m}\frac{\alpha}{s^2+\alpha^2} + sz(0) + z^{(1)}(0)$$

$$Z = \frac{F_0}{m}\frac{\alpha}{(s^2+\alpha^2)(s^2+\omega^2)} + \frac{sz(0)+z^{(1)}(0)}{s^2+\omega^2}$$
$$= \frac{F_0}{m}\frac{\alpha}{(s^2+\alpha^2)(s^2+\omega^2)} + \frac{sz(0)}{s^2+\omega^2} + \frac{z^{(1)}(0)}{s^2+\omega^2}$$

Take the terms separately

$$\frac{F_0}{m}\frac{\alpha}{(s^2+\alpha^2)(s^2+\omega^2)}$$

From the SWP software, this is Laplace transform of

$$\frac{F_0}{m}\frac{\alpha}{\sqrt{\alpha^2}\sqrt{\omega^2}(\alpha^2-\omega^2)}\left(\sqrt{\alpha^2}\sin t\sqrt{\omega^2} - \sqrt{\omega^2}\sin t\sqrt{\alpha^2}\right)$$
$$= \frac{F_0}{m}\frac{1}{\omega}\frac{1}{\left(\omega^2-\alpha^2\right)}\left[\omega\sin(\alpha t) - \alpha\sin(\omega t)\right]$$

For the next term

$$\frac{sz(0)}{s^2+\frac{k}{m}}$$

is Laplace transform of

$$z(0)\cos(\omega t)$$

For the final term

$$\frac{z^{(1)}(0)}{s^2+\omega^2}$$

is Laplace transform of

$$\frac{1}{\omega}z^{(1)}(0)\sin(\omega t)$$

The result is

$$z = z(0)\cos(\omega t) + \tfrac{1}{\omega}z^{(1)}(0)\sin(\omega t) + \frac{F_0}{m}\frac{1}{\omega}\frac{1}{\left(\omega^2-\alpha^2\right)}\left[\omega\sin(at) - \alpha\sin(\omega t)\right]$$

The case in the chapter was that $z(0) = 0$, so that

$$z = \frac{1}{\omega}z^{(1)}(0)\sin(\omega t) + \frac{F_0}{m}\frac{1}{\omega}\frac{1}{(\omega^2-\alpha^2)}\left[\omega\sin(\alpha t) - \alpha\sin(\omega t)\right]$$
$$= \left[\frac{1}{\omega}z^{(1)}(0) + \frac{F_0}{m}\frac{1}{\left(\omega^2-\alpha^2\right)}\right]\sin\omega t) + \frac{F_0}{m\left(\omega^2-\alpha^2\right)}\sin(\alpha t)$$

19. An object of mass m is subjected to an oscillating force in the x direction given by $F_0\sin(bt)$ where F_0 and b are constants. Find the solution to the equation of motion of the particle. Find the particular solution for the case that $x(0) = 0$ and $dx/dt = 0$ at $t = 0$.

$$m\frac{d^2x}{dt^2} = m\frac{dv}{dt} = F_0 a\sin(bt)$$

$$\frac{dv}{dt} = \frac{F_0}{m}\sin(bt)$$

$$v(t_1) = v(0) + \frac{F_0}{m}\int_0^{t_1}\sin(bt)dt$$
$$= v(0) - \frac{F_0}{bm}\cos(bt_1)|_0^{t_1}$$
$$= v(0) - \frac{F_0}{bm}\left[\cos(bt_1) - 1\right]$$

$$x(t_1) = x(0) + \int_0^{t_1}\left[v(0) - \frac{F_0}{bm}\cos(bt) + \frac{F_0}{bm}\right]dt$$
$$= x(0) + v(0)t_1 - \frac{F_0}{b^2m}\sin(bt)\Big|_0^{t_1} + \frac{F_0}{bm}t_1$$
$$= x(0) + v(0)t_1 - \frac{F_0}{b^2m}\sin(bt_1) + \frac{F_0}{bm}t_1$$
$$x(t) = x(0) + \left[v(0) + \frac{F_0}{bm}\right]t - \frac{F_0}{b^2m}\sin(bt)$$

For the case that $x(0) = 0$ and $dx/dt = 0$ at $t = 0$.

$$x(t) = \frac{F_0}{bm}t - \frac{F_0}{b^2m}\sin(bt) = \frac{F_0}{bm}\left[t - \frac{1}{b}\sin(bt)\right]$$

20. An object of mass m is subjected to a gradually increasing force given by $a(1-e^{-bt})$ where a and b are constants. Solve the equation of motion of the particle. Find the particular solution for the case that $x(0) = 0$ and $dx/dt = 0$ at $t = 0$.

$$m\frac{d^2x}{dt^2} = m\frac{dv}{dt} = F_0(1-e^{-bt})$$

$$\frac{dv}{dt} = \frac{F_0}{m}(1-e^{-bt})$$

$$v(t_1) = v(0) + \frac{F_0}{m}\int_0^{t_1}(1-e^{-bt})dt = v(0) + \frac{F_0}{bm}\left[t + \frac{1}{b}e^{-bt}\right]\Big|_0^{t_1}$$
$$= v(0) + \frac{F_0}{bm}\left[t_1 + \frac{1}{b}e^{-bt_1} - \frac{1}{b}\right]$$

$$x(t_1) = x(0) + \int_0^{t_1} v(0)\mathrm{d}t + \frac{F_0}{bm}\int_0^{t_1} \left[t + \frac{1}{b}e^{-bt} - \frac{1}{b}\right]\mathrm{d}t$$

$$= x(0) + v(0)t_1 + \frac{F_0}{bm}\left[\frac{t^2}{2} - \frac{1}{b^2}e^{-bt} - \frac{t}{b}\right]\Bigg|_0^{t_1}$$

$$= x(0) + v(0)t_1 + \frac{F_0}{bm}\left[\frac{t_1^2}{2} - \frac{1}{b^2}(e^{-bt_1} - 1) - \frac{t_1}{b}\right]$$

In the case that $x(0) = 0$ and $\mathrm{d}x/\mathrm{d}t = 0$ at $t = 0$.

$$x(t) = \frac{F_0}{bm}\left[\frac{t_1^2}{2} - \frac{1}{b^2}(e^{-bt_1} - 1) - \frac{t_1}{b}\right]$$

Chapter 13

Operators, Matrices, and Group Theory

EXERCISES

Exercise 13.1. Find the eigenfunctions and eigenvalues of the operator $i\dfrac{\mathrm{d}}{\mathrm{d}x}$, where $i = \sqrt{-1}$.

$$i\frac{\mathrm{d}f}{\mathrm{d}x} = af$$

Separate the variables:

$$\begin{aligned}\frac{\mathrm{d}f}{\mathrm{d}x}\mathrm{d}x &= \frac{\mathrm{d}f}{f} = \frac{a}{i} = -ia\\ \ln(f) &= -iax + C\\ f &= e^C e^{-iax} = Ae^{-iax}\\ \frac{\mathrm{d}f}{\mathrm{d}x} &= -iaAe^{-iax} = -iaf\end{aligned}$$

The single eigenfunction is Ae^{-iax} and the eigenvalue is $-ia$. Since no boundary conditions were specified, the constants A and a can take on any values.

Exercise 13.2. Find the operator equal to the operator product $\dfrac{\mathrm{d}^2}{\mathrm{d}x^2}x$.

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}x^2}xf &= \frac{\mathrm{d}}{\mathrm{d}x}\left[x\frac{\mathrm{d}f}{\mathrm{d}x} + f\right] = x\frac{\mathrm{d}^2f}{\mathrm{d}x^2} + \frac{\mathrm{d}f}{\mathrm{d}x} + \frac{\mathrm{d}f}{\mathrm{d}x}\\ &= x\frac{\mathrm{d}^2f}{\mathrm{d}x^2} + 2\frac{\mathrm{d}f}{\mathrm{d}x}\end{aligned}$$

The operator equation is

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}x = x\frac{\mathrm{d}^2}{\mathrm{d}x^2} + 2\frac{\mathrm{d}}{\mathrm{d}x}$$

Exercise 13.3. Find the commutator $[x^2, \dfrac{\mathrm{d}^2}{\mathrm{d}x^2}]$.

$$\begin{aligned}[x^2, \frac{\mathrm{d}^2}{\mathrm{d}x^2}]f &= x^2\frac{\mathrm{d}^2}{\mathrm{d}x^2}f - \frac{\mathrm{d}^2}{\mathrm{d}x^2}(x^2 f)\\ &= x^2\frac{\mathrm{d}^2f}{\mathrm{d}x^2} - \frac{\mathrm{d}}{\mathrm{d}x}\left(2xf + x^2\frac{\mathrm{d}f}{\mathrm{d}x}\right)\\ &= x^2\frac{\mathrm{d}^2f}{\mathrm{d}x^2} - 2f - 2x\frac{\mathrm{d}f}{\mathrm{d}x} - x^2\frac{\mathrm{d}^2f}{\mathrm{d}x^2}\\ &= -2f - 2x\frac{\mathrm{d}f}{\mathrm{d}x}\\ \left[x^2, \frac{\mathrm{d}^2}{\mathrm{d}x^2}\right] &= -2 - 2x\frac{\mathrm{d}}{\mathrm{d}x}\end{aligned}$$

Exercise 13.4. If $\widehat{A} = x + \dfrac{\mathrm{d}}{\mathrm{d}x}$, find $\widehat{A}^3$.

$$\begin{aligned}\widehat{A}^3 &= \left(x + \frac{\mathrm{d}}{\mathrm{d}x}\right)\left(x + \frac{\mathrm{d}}{\mathrm{d}x}\right)\left(x + \frac{\mathrm{d}}{\mathrm{d}x}\right)\\ &= \left(x + \frac{\mathrm{d}}{\mathrm{d}x}\right)\left(x^2 + \frac{\mathrm{d}}{\mathrm{d}x}x + x\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)\\ &= x^3 + x\frac{\mathrm{d}}{\mathrm{d}x}x + x^2\frac{\mathrm{d}}{\mathrm{d}x} + x\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{\mathrm{d}}{\mathrm{d}x}x^2 + \frac{\mathrm{d}^2}{\mathrm{d}x^2}x\\ &\quad + \frac{\mathrm{d}}{\mathrm{d}x}x\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\mathrm{d}^3}{\mathrm{d}x^3}.\end{aligned}$$

Exercise 13.5. Find an expression for $\widehat{B}^2$ if $\widehat{B} = x(\mathrm{d}/\mathrm{d}x)$ and find $\widehat{B}^2 f$ if $f = bx^4$.

$$\begin{aligned}\widehat{B}^2 f &= \left(x\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 f = x\frac{\mathrm{d}}{\mathrm{d}x}\left(x\frac{\mathrm{d}f}{\mathrm{d}x}\right)\\ &= x\left(\frac{\mathrm{d}f}{\mathrm{d}x} + x\frac{\mathrm{d}^2f}{\mathrm{d}x^2}\right) = x\frac{\mathrm{d}f}{\mathrm{d}x} + x^2\frac{\mathrm{d}^2f}{\mathrm{d}x^2}\\ \widehat{B}^2(bx^4) &= \left(x\frac{\mathrm{d}f}{\mathrm{d}x} + x^2\frac{\mathrm{d}^2f}{\mathrm{d}x^2}\right)bx^4\\ &= 4bx^4 + x^2(4)(3)bx^2 = 16bx^4\end{aligned}$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00037-9

Exercise 13.6. Show that the solution in the previous example satisfies the original equation.

$$\frac{d^2y}{dx^2} - 3\frac{dy}{dx} + 2y = 0$$
$$\frac{d^2}{dx^2}\left(c_1e^{2x} + c_2e^x\right) - 3\frac{d}{dx}\left(c_1e^{2x} + c_2e^x\right)$$
$$+2\left(c_1e^{2x} + c_2e^x\right)$$
$$= 4c_1e^{2x} + c_2e^x - 3\left(2c_1e^{2x} + c_2e^x\right)$$
$$+2\left(c_1e^{2x} + c_2e^x\right) = 0$$

Exercise 13.7. Find the eigenfunction of the Hamiltonian operator for motion in the x direction if $\mathcal{V}(x) = E_0 =$ constant.

$$\left[-\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2} + \dot{E}_0\right]\psi = E\psi$$
$$\frac{\partial^2\psi}{\partial x^2} = -\frac{2m}{\hbar}\left(E - E_0\right)\psi = -\kappa^2\psi$$

where we let

$$\kappa^2 = \frac{2m}{\hbar}(E - E_0)$$

If $E \succ E_0$ the real solution is

$$\psi_{\text{real}} = c_1\sin(\kappa x) + c_2\cos(\kappa x)$$

In order for ψ_{real} to be an eigenfunction, either c_1 or c_2 has to vanish. Another version of the solution is

$$\psi_{\text{complex}} = b_1e^{i\kappa x} + b_2e^{-i\kappa x}$$

In order for ψ_{complex} to be an eigenfunction, either b_1 or b_2 has to vanish.

Exercise 13.8. Show that the operator for the momentum in Eq. (13.19) is hermitian.

We integrate by parts

$$\frac{\hbar}{i}\int_{-\infty}^{\infty}\chi^*\frac{d\psi}{dx}dx = \frac{\hbar}{i}\chi^*\psi\Big|_{-\infty}^{\infty} - \frac{\hbar}{i}\int_{-\infty}^{\infty}\frac{d\chi^*}{dx}\psi\,dx$$
$$= -\frac{\hbar}{i}\int_{-\infty}^{\infty}\frac{d\chi^*}{dx}\psi\,dx$$

The other side of the equation is, after taking the complex conjugate of the operator

$$-\frac{\hbar}{i}\int_{-\infty}^{\infty}\frac{d\chi^*}{dx}\psi\,dx$$

which is the same expression.

Exercise 13.9. Write an equation similar to Eq. (13.20) for the $\hat{\sigma}_v$ operator whose symmetry element is the y-z plane.

$$\hat{\sigma}_{v(yz)}(x_1, y_1, z_1) = (-\,x_1, y_1, z_1)$$

Exercise 13.10. Find $\widehat{C}_{2(x)}(1,2,-3)$.

$$\widehat{C}_{2(z)}(1,2,-3) = (-1,-2,-3)$$

Exercise 13.11. Find $\widehat{S}_{2(y)}(3,4,5)$.

$$\widehat{S}_{2(y)}(3,4,5) = (-3.-4,-5)$$

Exercise 13.12. List the symmetry elements of a uniform cube centered at the origin with its faces perpendicular to the coordinate axes.

The inversion center at the origin.
Three C_4 axes coinciding with the coordinate axes.
Four C_3 axes passing through opposite corners of the cube.
Four S_6 axes coinciding with the C_3 axes.
Six C_2 axes connecting the midpoints of opposite edges.
Three mirror planes in the coordinate planes.
Six mirror planes passing through opposite edges.

Exercise 13.13. List the symmetry elements for

a. H_2O (bent)
$E, C_{2(z)}, \sigma_{xz}, \sigma_{yz}$
b. CO_2 (linear)
$E, i, \sigma_h, C_{\infty(z)}, \infty C_2, \sigma_h, \infty\sigma_v$

Exercise 13.14. Find $\widehat{i}\psi_{2px}$ where $\widehat{i}$ is the inversion operator. Show that ψ_{2px} is an eigenfunction of the inversion operator, and find its eigenvalue.

$$\widehat{i}\psi_{2px} = \widehat{i}\left\{x\exp\left[\frac{-(x^2+y^2+z^2)^{1/2}}{2a_0}\right]\right\}$$
$$= -x\exp\left[\frac{-(x^2+y^2+z^2)^{1/2}}{2a_0}\right] = -\psi_{2px}$$

The eigenvalue is equal to -1.

Exercise 13.15. The potential energy of two charges Q_1 and Q_2 in a vacuum is

$$\mathcal{V} = \frac{Q_1Q_2}{4\pi\epsilon_0 r_{12}}$$

where r_{12} is the distance between the charges and ε_0 is a constant called the permittivity of a vacuum, equal to $8.854187817 \times 10^{-12}$ $\text{Fm}^{-1} = 8.854187817 \times 10^{-12}$ $\text{C}^2\text{N}^{-1}\text{m}^{-2}$. The potential energy of a hydrogen molecules is given by

$$\mathcal{V} = \frac{e^2}{4\pi\epsilon_0 r_{AB}} - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}}$$
$$-\frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where A and B represent the nuclei and 1 and 2 represent the electrons, and where the two indexes indicate the two particles whose interparticle distance is denoted. If a hydrogen molecule is placed so that the origin is midway between the two nuclei and the nuclei are on the z axis, show that the inversion operator $\hat{\imath}$ and the reflection operator $\hat{\sigma}_h$ do not change the potential energy if applied to the electrons but not to the nuclei.

We use the fact that the origin is midway between the nuclei. Under the inversion operation, electron 1 is now the same distance from nucleus A as it was originally from nucleus B, and the same is true of electron 2. Under the $\hat{\sigma}_h$ operation, the same is true. The potential energy function is unchanged under each of these operations.

Exercise 13.16. Find the product

$$\begin{bmatrix} 1 & 0 & 2 \\ 0 & -1 & 1 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 3 \\ 1 \end{bmatrix} = \begin{bmatrix} 2 \\ -2 \\ 1 \end{bmatrix}$$

Exercise 13.17. Find the two matrix products

$$\begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 1 & -1 & 2 \end{bmatrix} \begin{bmatrix} 1 & 3 & 2 \\ 2 & 2 & -1 \\ -2 & 1 & -1 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 1 & 3 & 2 \\ 2 & 2 & -1 \\ -2 & -1 & -1 \end{bmatrix} \times \begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 1 & -1 & 2 \end{bmatrix}$$

The left factor in one product is equal to the right factor in the other product, and vice versa. Are the two products equal to each other?

$$\begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 1 & -1 & 2 \end{bmatrix} \begin{bmatrix} 1 & 3 & 2 \\ 2 & 2 & -1 \\ -2 & 1 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 10 & -3 \\ 5 & 14 & 3 \\ -5 & 3 & 1 \end{bmatrix}$$

$$\begin{bmatrix} 1 & 3 & 2 \\ 2 & 2 & -1 \\ -2 & -1 & -1 \end{bmatrix} \begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 1 & -1 & 2 \end{bmatrix} = \begin{bmatrix} 12 & 6 & 10 \\ 7 & 9 & 6 \\ -6 & -5 & -9 \end{bmatrix}.$$

The two products are not equal to each other.

Exercise 13.18. Show that the properties of Eqs. (13.45) and (13.46) are obeyed by the particular matrices

$$\mathbf{A} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \quad \mathbf{B} = \begin{bmatrix} 0 & 2 & 2 \\ -3 & 1 & 2 \\ 1 & -2 & -3 \end{bmatrix} \times \mathbf{C} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 3 & -2 \\ 2 & 7 & -7 \end{bmatrix}$$

$$\mathbf{BC} = \begin{bmatrix} 0 & 2 & 2 \\ -3 & 1 & 2 \\ 1 & -2 & -3 \end{bmatrix} \begin{bmatrix} 1 & 0 & 1 \\ 0 & 3 & -2 \\ 2 & 7 & -7 \end{bmatrix} = \begin{bmatrix} 4 & 20 & -18 \\ 1 & 17 & -19 \\ -5 & -27 & 26 \end{bmatrix}$$

$$\mathbf{A(BC)} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \begin{bmatrix} 4 & 20 & -18 \\ 1 & 17 & -19 \\ -5 & -27 & 26 \end{bmatrix} = \begin{bmatrix} -9 & -27 & 22 \\ -9 & 3 & -11 \\ -9 & 33 & -44 \end{bmatrix}$$

$$\mathbf{AB} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \begin{bmatrix} 0 & 2 & 2 \\ -3 & 1 & 2 \\ 1 & -2 & -3 \end{bmatrix} = \begin{bmatrix} -3 & -2 & -3 \\ -9 & 1 & 0 \\ -15 & 4 & 3 \end{bmatrix}$$

$$\mathbf{(AB)C} = \begin{bmatrix} -3 & -2 & -3 \\ -9 & 1 & 0 \\ -15 & 4 & 3 \end{bmatrix} \begin{bmatrix} 1 & 0 & 1 \\ 0 & 3 & -2 \\ 2 & 7 & -7 \end{bmatrix} = \begin{bmatrix} -9 & -27 & 22 \\ -9 & 3 & -11 \\ -9 & 33 & -44 \end{bmatrix}.$$

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \left(\begin{bmatrix} 0 & 2 & 2 \\ -3 & 1 & 2 \\ 1 & -2 & -3 \end{bmatrix} + \begin{bmatrix} 1 & 0 & 1 \\ 0 & 3 & -2 \\ 2 & 7 & -7 \end{bmatrix} \right) = \begin{bmatrix} 4 & 25 & -27 \\ 7 & 58 & -48 \\ 10 & 91 & -69 \end{bmatrix}$$

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \begin{bmatrix} 0 & 2 & 2 \\ -3 & 1 & 2 \\ 1 & -2 & -3 \end{bmatrix} + \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \begin{bmatrix} 1 & 0 & 1 \\ 0 & 3 & -2 \\ 2 & 7 & -7 \end{bmatrix}$$

$$= \begin{bmatrix} -3 & -2 & -3 \\ -9 & 1 & 0 \\ -15 & 4 & 3 \end{bmatrix} + \begin{bmatrix} 7 & 27 & -24 \\ 16 & 57 & -48 \\ 25 & 87 & -72 \end{bmatrix} = \begin{bmatrix} 4 & 25 & -27 \\ 7 & 58 & -48 \\ 10 & 91 & -69 \end{bmatrix}$$

Exercise 13.19. Show by explicit matrix multiplication that

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{31} & a_{41} \\ a_{31} & a_{31} & a_{31} & a_{41} \\ a_{41} & a_{41} & a_{31} & a_{41} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{21} & a_{31} & a_{41} \\ a_{31} & a_{31} & a_{31} & a_{41} \\ a_{41} & a_{41} & a_{31} & a_{41} \end{bmatrix}.$$

:Each element is produces as a single term since the other terms in the same contain a factor zero.

Exercise 13.20. Show that $\mathbf{AA}^{-1} = \mathbf{E}$ and that $\mathbf{A}^{-1}\mathbf{A} = \mathbf{E}$ for the matrices of the preceding example.

Mathematica and other software packages can find a matrix product with a single command. Using the Scientific Work Place software

$$\mathbf{AA}^{-1} = \begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix} \begin{bmatrix} \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \\ \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{A}^{-1}\mathbf{A} = \begin{bmatrix} \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \\ \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{bmatrix} \begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Exercise 13.21. Use Mathematica or another software package to verify the inverse found in the preceding example. Using the Scientific Work Place software

$$\begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix}^{-1} = \begin{bmatrix} \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \\ \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{bmatrix}$$

Exercise 13.22. Find the inverse of the matrix

$$\mathbf{A} = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}$$

Using the Scientific Work Place software,

$$\mathbf{A}^{-1} = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}^{-1} = \begin{bmatrix} -2 & 1 \\ \frac{3}{2} & -\frac{1}{2} \end{bmatrix}$$

Check this

$$\begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix} \begin{bmatrix} -2 & 1 \\ \frac{3}{2} & -\frac{1}{2} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Exercise 13.23. Expand the following determinant by minors:

$$\begin{vmatrix} 3 & 2 & 0 \\ 7 & -1 & 5 \\ 2 & 3 & 4 \end{vmatrix} = 3\begin{vmatrix} -1 & 5 \\ 3 & 4 \end{vmatrix} - 2\begin{vmatrix} 7 & 5 \\ 2 & 4 \end{vmatrix}$$

$$= 3(-4 - 15) - 2(28 - 10) = -93$$

Exercise 13.24. a. Find the value of the determinant

$$\begin{vmatrix} 3 & 4 & 5 \\ 2 & 1 & 6 \\ 3 & -5 & 10 \end{vmatrix} = 47$$

b. Interchange the first and second columns and find the value of the resulting determinant.

$$\begin{vmatrix} 4 & 3 & 5 \\ 1 & 2 & 6 \\ -5 & 3 & 10 \end{vmatrix} = -47$$

c. Replace the second column by the sum of the first and second columns and find the value of the resulting determinant.

$$\begin{vmatrix} 7 & 4 & 5 \\ 3 & 1 & 6 \\ -2 & -5 & 10 \end{vmatrix} = 47$$

d. Replace the second column by the first, thus making two identical columns, and find the value of the resulting determinant.

$$\begin{vmatrix} 3 & 3 & 5 \\ 2 & 2 & 6 \\ 3 & 3 & 10 \end{vmatrix} = 0$$

Exercise 13.25. Obtain the inverse of the following matrix by hand. Then use Mathematica to verify your answer.

$$\begin{bmatrix} 1 & 3 & 0 \\ 3 & 0 & 4 \\ 1 & 2 & 0 \end{bmatrix}^{-1} = \begin{bmatrix} -2 & 0 & 3 \\ 1 & 0 & -1 \\ \frac{3}{2} & \frac{1}{4} & -\frac{9}{4} \end{bmatrix}$$

$$\begin{bmatrix} 1 & 3 & 0 \\ 3 & 0 & 4 \\ 1 & 2 & 0 \end{bmatrix} \begin{bmatrix} -2 & 0 & 3 \\ 1 & 0 & -1 \\ \frac{3}{2} & \frac{1}{4} & -\frac{9}{4} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Exercise 13.26. Obtain the multiplication table for the C_{2v} point group and show that it satisfies the conditions to be a group.

Think of the H_2O molecule, which possesses all of the symmetry operators in this group. Place the molecule in the $y-z$ plane with the rotation axis on the z axis. Note that in this group, each element is its own inverse. For the other operators, one inspects the action of the right-most operator, followed by the action of the left-most operator. If the result is ambiguous, you need to use the fact that a reflection changes a right-handed system to a left-handed system while the rotation does not. For example, $\widehat{\sigma}_{v(yz)}$ followed by $\widehat{\sigma}_{v(xz)}$ exchanges the hydrogens, but changes the handedness of a coordinate system, so the result is the same as $\widehat{\sigma}_{v(xz)}$.

	$\widehat{E}$	$\widehat{C}_2$	$\widehat{\sigma}_{v(yz)}$	$\widehat{\sigma}_{v(xz)}$
$\widehat{E}$	$\widehat{E}$	$\widehat{C}_2$	$\widehat{\sigma}_{v(yz)}$	$\widehat{\sigma}_{v(xz)}$
$\widehat{C}_2$	$\widehat{C}_2$	$\widehat{E}$	$\widehat{\sigma}_{v(xz)}$	$\widehat{\sigma}_{v(yz)}$
$\widehat{\sigma}_{v(yz)}$	$\widehat{\sigma}_{v(yz)}$	$\widehat{\sigma}_{v(xz)}$	$\widehat{E}$	$\widehat{C}_2$
$\widehat{\sigma}_{v(xz)}$	$\widehat{\sigma}_{v(xz)}$	$\widehat{\sigma}_{v(xz)}$	$\widehat{C}_2$	$\widehat{E}$

These operators form a group because (1) each product is a member of the group; (2) the group does include the identity operator; (3) because each of the members is its own inverse; and (4) multiplication is associative.

Exercise 13.27.

a. Find the matrix equivalent to $\widehat{C}_2(z)$.

$$x' = -x$$
$$y' = -y$$
$$z' = z$$
$$\widehat{C}_2(z) \leftrightarrow \begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix}$$

b. Find the matrix equivalent to $\widehat{S}_3(z)$.

$$x' = \cos(2\pi/3)x - \sin(2\pi/3)y = -\frac{1}{2}x - \left(\frac{1}{2}\sqrt{3}\right)y$$
$$y' = \sin(2\pi/3)x + \cos(2\pi/3)y = \left(\frac{1}{2}\sqrt{3}\right)x - \frac{1}{2}y$$
$$z' = z.$$
$$\widehat{S}_3(z) \leftrightarrow \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

c. Find the matrix equivalent to $\hat{\sigma}_h$.

$$x' = x$$
$$y' = y$$
$$z' = -z$$
$$\hat{\sigma}_h \leftrightarrow \begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{matrix}$$

Exercise 13.28. By transcribing Table 13.1 with appropriate changes in symbols, generate the multiplication table for the matrices in Eq. (13.65).

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	B	E	F	C	D
B	B	E	A	D	F	C
C	C	D	F	E	A	B
D	D	D	F	C	E	A
F	F	C	D	A	B	E

Exercise 13.29. Verify several of the entries in the multiplication table by matrix multiplication of the matrices in Eq. (13.65).

$$\mathbf{AB} = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{E}$$

$$\mathbf{AD} = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{C}$$

$$\mathbf{CD} = \begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{A}$$

Exercise 13.30. Show by matrix multiplication that two matrices with a 2 by 2 block and two 1 by 1 blocks produce another matrix with a 2 by 2 block and two 1 by 1 blocks when multiplied together.

$$\begin{bmatrix} a & b & 0 & 0 \\ c & d & 0 & 0 \\ 0 & 0 & e & 0 \\ 0 & 0 & 0 & f \end{bmatrix}\begin{bmatrix} \alpha & \beta & 0 & 0 \\ \gamma & \delta & 0 & 0 \\ 0 & 0 & \varepsilon & 0 \\ 0 & 0 & 0 & \phi \end{bmatrix} = \begin{bmatrix} a\alpha + b\gamma & a\beta + b\delta & 0 & 0 \\ c\alpha + d\gamma & c\beta + d\delta & 0 & 0 \\ 0 & 0 & \varepsilon e & 0 \\ 0 & 0 & 0 & f\phi \end{bmatrix}$$

Exercise 13.31. Pick a few pairs of 2 by 2 submatrices from Eq. (13.65) and show that they multiply in the same way as the 3 by 3 matrices.

$$\begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}\begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}\begin{bmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{bmatrix}$$

$$\begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}\begin{bmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{bmatrix}.$$

Exercise 13.32. Show that the 1 by 1 matrices (scalars) in Eq. (13.67) obey the same multiplication table as does the group of symmetry operators.

Since the elements $\widehat{E} \leftrightarrow 1$ $\widehat{C}_3 \leftrightarrow 1$ $\widehat{C}_3^2 \leftrightarrow 1$, the product of any two of these will yield $+1$. Since $\hat{\sigma}_a \leftrightarrow -1$ $\hat{\sigma}_b \leftrightarrow -1$ $\hat{\sigma}_c \leftrightarrow -1$, the product of any two of these will yield 1. The product of any of the first three with any of the second three will yield -1. the multiplication table is

	$\widehat{E}$	$\widehat{C}_3$	$\widehat{C}_3^2$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\hat{\sigma}_c$
$\widehat{E}$	1	1	1	−1	−1	−1
$\widehat{C}_3$	1	1	1	−1	−1	−1
$\widehat{C}_3^2$	1	1	1	−1	−1	−1
$\hat{\sigma}_a$	−1	−1	−1	1	1	1
$\hat{\sigma}_b$	−1	−1	−1	1	1	1
$\hat{\sigma}_c$	−1	−1	−1	1	1	1

PROBLEMS

1. Find the following commutators, where $D_x = \mathrm{d}/\mathrm{d}x$:

a. $\left[\frac{\mathrm{d}}{\mathrm{d}x}, \sin(x)\right]$;

$$\left[\frac{\mathrm{d}}{\mathrm{d}x}, \sin(x)\right] f = \frac{\mathrm{d}}{\mathrm{d}x}[\sin(x) f] - \sin(x)\frac{\mathrm{d}f}{\mathrm{d}x}$$

$$= \cos(x) f + \sin(x)\frac{\mathrm{d}f}{\mathrm{d}x}$$

$$- \sin(x)\frac{\mathrm{d}f}{\mathrm{d}x} = \cos(x) f$$

$$\left[\frac{\mathrm{d}}{\mathrm{d}x}, \sin(x)\right] = \cos(x)$$

b. $\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}, x\right]$;

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}, x\right] f = \frac{\mathrm{d}^2}{\mathrm{d}x^2}[xf] - x\frac{\mathrm{d}^2}{\mathrm{d}x^2} f$$

$$= \frac{\mathrm{d}}{\mathrm{d}x}\left[x\frac{\mathrm{d}f}{\mathrm{d}x} + f\right] - x\frac{\mathrm{d}^2}{\mathrm{d}x^2} f$$

$$= \frac{\mathrm{d}f}{\mathrm{d}x} + x\frac{\mathrm{d}^2}{\mathrm{d}x^2} f + \frac{\mathrm{d}f}{\mathrm{d}x} - x\frac{\mathrm{d}^2}{\mathrm{d}x^2} f$$

$$= 2\frac{\mathrm{d}f}{\mathrm{d}x}$$

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}, x\right] = 2\frac{\mathrm{d}}{\mathrm{d}x}$$

2. Find the following commutators, where $D_x = \mathrm{d}/\mathrm{d}x$:

a. $\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}, x^2\right]$;

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}, x^2\right] f = \frac{\mathrm{d}^2}{\mathrm{d}x^2},[x^2 f] - x^2\frac{\mathrm{d}^2 f}{\mathrm{d}f^2}$$

$$= \frac{\mathrm{d}}{\mathrm{d}x}\left[2xf + x^2\frac{\mathrm{d}f}{\mathrm{d}x}\right] - x^2\frac{\mathrm{d}^2 f}{\mathrm{d}f^2}$$

$$= +2x\frac{\mathrm{d}f}{\mathrm{d}x} + 2f + 2x\frac{\mathrm{d}f}{\mathrm{d}x} + x^2\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}$$

$$-x^2\frac{\mathrm{d}^2 f}{\mathrm{d}f^2}$$

$$= 4x\frac{\mathrm{d}f}{\mathrm{d}x} + 2f$$

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}, x^2\right] = 4x\frac{\mathrm{d}}{\mathrm{d}x} + 2$$

b. $\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}, g(x)\right]$.

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}, g(x)\right] f = \frac{\mathrm{d}^2}{\mathrm{d}x^2}[g(x) f(x)] - g(x)\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}$$

$$= \frac{\mathrm{d}}{\mathrm{d}x}\left[g\frac{\mathrm{d}f}{\mathrm{d}x} + f\frac{\mathrm{d}g}{\mathrm{d}x}\right] - g(x)\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}$$

$$= g\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} + \frac{\mathrm{d}f}{\mathrm{d}x}\frac{\mathrm{d}g}{\mathrm{d}x} + \frac{\mathrm{d}f}{\mathrm{d}x}\frac{\mathrm{d}g}{\mathrm{d}x}$$

$$+g(x)\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} - g(x)\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}$$

$$= g\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} + 2\frac{\mathrm{d}f}{\mathrm{d}x}\frac{\mathrm{d}g}{\mathrm{d}x}$$

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}, g(x)\right] = g\frac{\mathrm{d}^2}{\mathrm{d}x^2} + 2\left(\frac{\mathrm{d}g}{\mathrm{d}x}\right)\frac{\mathrm{d}}{\mathrm{d}x}$$

3. The components of the angular momentum correspond to the quantum mechanical operators:

$$\widehat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \quad \widehat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),$$
$$\widehat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

These operators do not commute with each other. Find the commutator $\left[\widehat{L}_x, \widehat{L}_y\right]$.

$$\begin{aligned}
&\left[\widehat{L}_x, \widehat{L}_y\right] f \\
&= \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) f \\
&\quad - \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) f \\
&= -\hbar^2\left[y\frac{\partial}{\partial z}z\frac{\partial f}{\partial x} - y\frac{\partial}{\partial z}x\frac{\partial f}{\partial z} - z\frac{\partial}{\partial y}z\frac{\partial f}{\partial x}\right. \\
&\quad + z\frac{\partial}{\partial y}x\frac{\partial f}{\partial z} - z\frac{\partial}{\partial x}y\frac{\partial f}{\partial z} + z\frac{\partial}{\partial x}z\frac{\partial f}{\partial y} \\
&\quad \left. - x\frac{\partial}{\partial z}z\frac{\partial f}{\partial y} + x\frac{\partial}{\partial z}y\frac{\partial f}{\partial z}\right] \\
&= -\hbar^2\left[yz\frac{\partial^2 f}{\partial z\partial x} + y\frac{\partial f}{\partial z} - xy\frac{\partial^2 f}{\partial z^2} - z^2\frac{\partial^2 f}{\partial y\partial x}\right. \\
&\quad + zx\frac{\partial^2 f}{\partial y\partial z} - zy\frac{\partial^2 f}{\partial x\partial z} + z^2\frac{\partial^2 f}{\partial x\partial y} \\
&\quad \left. + zy\frac{\partial^2 f}{\partial z^2} - x\frac{\partial f}{\partial y} - xz\frac{\partial^2 f}{\partial z\partial y}\right]
\end{aligned}$$

We can now apply Euler's reciprocity relation to cancel all of the terms but two:

$$\begin{aligned}
\left[\widehat{L}_x, \widehat{L}_y\right] f &= -\hbar^2\left[y\frac{\partial f}{\partial z} - x\frac{\partial f}{\partial y}\right] \\
&= \hbar^2\left[x\frac{\partial f}{\partial y} - y\frac{\partial f}{\partial z}\right] = i\hbar\widehat{L}_z
\end{aligned}$$

4. The Hamiltonian operator for a one-dimensional harmonic oscillator moving in the x direction is

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{kx^2}{2}.$$

Find the value of the constant a such that the function e^{-ax^2} is an eigenfunction of the Hamiltonian operator and find the eigenvalue E. The quantity k is the force constant, m is the mass of the oscillating panicle, and $\hbar$ is Planck's constant divided by 2π.

$$\begin{aligned}
&-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 e^{-ax^2}}{\mathrm{d}x^2} + \frac{kx^2 e^{-ax^2}}{2} \\
&= -\frac{\hbar^2}{2m}\frac{\mathrm{d}}{\mathrm{d}x}\left(-2axe^{-ax^2}\right) \\
&\quad + \frac{kx^2 e^{-ax^2}}{2} = Ee^{-ax^2} \\
&= -\frac{\hbar^2}{2m}\left(-2ae^{-ax^2} + 4a^2x^2e^{-ax^2}\right) \\
&\quad + \frac{kx^2 e^{-ax^2}}{2} = Ee^{-ax^2}
\end{aligned}$$

Divide by e^{-ax^2}

$$= -\frac{\hbar^2}{2m}(-2a + 4a^2x^2) + \frac{kx^2}{2} = E$$

The coefficients of x^2 on the two sides of the equation must be equal:

$$\begin{aligned}
\frac{\hbar^2}{2m}(4a^2x^2) &= \frac{kx^2}{2} \\
a^2 &= \frac{mk}{4\hbar^2} \\
a &= \frac{\sqrt{mk}}{2\hbar}
\end{aligned}$$

The constant terms on the two sides of the equation must be equal:

$$E = \frac{\hbar^2 a}{m} = \frac{\hbar^2}{2m\hbar}(mk)^{1/2} = \frac{\hbar}{2}\sqrt{\frac{k}{m}} = \frac{1}{2}h\nu$$

where ν is the frequency of the classical oscillator.

5. In quantum mechanics, the expectation value of a mechanical quantity is given by

$$\langle A\rangle = \frac{\int \psi^*\widehat{A}\psi\,\mathrm{d}x}{\int \psi^*\psi\,\mathrm{d}x},$$

where $\widehat{A}$ is the operator for the mechanical quantity and ψ is the wave function for the state of the system. The integrals are over all permitted values of the coordinates of the system. The expectation value is defined as the prediction of the mean of a large number of measurements of the mechanical quantity, given that the system is in the state corresponding to ψ prior to each measurement.

For a particle moving in the x direction only and confined to a region on the x axis from $x = 0$ to $x = a$, the integrals are single integrals from 0 to a and $\hat{p}_x$ is given by $(\hbar/i)\partial/\partial x$. The normalized wave function is

$$\psi = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)$$

Normalization means that the integral in the denominator of the expectation value expression is equal to unity.

a. Show that this wave function is normalized. We let $u = \pi x/a$

$$\frac{2}{a}\int_0^a \sin^2\left(\frac{\pi x}{a}\right)\mathrm{d}x = \frac{2}{a}\frac{a}{\pi}\int_0^\pi \sin^2(u)\,\mathrm{d}u$$
$$= \frac{2}{\pi}\left[\frac{x}{2} - \frac{\sin(2x)}{4}\right]\Bigg|_0^\pi = \frac{2}{\pi}\frac{\pi}{2} = 1$$

b. Find the expectation value of x.

$$\langle x\rangle = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)x\sin\left(\frac{\pi x}{a}\right)\mathrm{d}x$$
$$= \frac{2}{a}\int_0^a x\sin^2\left(\frac{\pi x}{a}\right)\mathrm{d}x$$
$$= \frac{2}{a}\left(\frac{a}{\pi}\right)^2\int_0^\pi u\sin^2(u)\,du$$
$$= \frac{2a}{\pi^2}\left[\frac{x^2}{4} - \frac{x\sin(2x)}{4} - \frac{\cos(2x)}{8}\right]\Bigg|_0^\pi$$
$$= \frac{2a}{\pi^2}\left[\frac{\pi^2}{4} - \frac{1}{8} + \frac{1}{8}\right] = \frac{a}{2}$$

c. The operator corresponding to p_x is $\left(\frac{\hbar}{i}\right)\frac{\mathrm{d}}{\mathrm{d}x}$. Find the expectation value of p_x.

$$\langle p_x\rangle = \left(\frac{\hbar}{i}\right)\frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\frac{\mathrm{d}}{\mathrm{d}x}\sin\left(\frac{\pi x}{a}\right)\mathrm{d}x$$
$$= \frac{2\hbar}{ia}\frac{\pi}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\cos\left(\frac{\pi x}{a}\right)\mathrm{d}x$$
$$= \frac{2\hbar}{ia}\frac{\pi}{a}\frac{a}{\pi}\int_0^\pi \sin(u)\cos(u)\mathrm{d}u$$
$$= \frac{2\hbar}{ia}\frac{\sin(u)}{2}\Bigg|_0^\pi = 0$$

d. Find the expectation value of p_x^2.

$$\langle p_x^2\rangle = -\hbar^2\frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\sin\left(\frac{\pi x}{a}\right)\mathrm{d}x$$
$$= -\hbar\frac{2}{a}\frac{\pi}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\frac{\mathrm{d}}{\mathrm{d}x}\cos\left(\frac{\pi x}{a}\right)\mathrm{d}x$$
$$= \hbar^2\frac{2}{a}\left(\frac{\pi}{a}\right)^2\int_0^a \sin^2\left(\frac{\pi x}{a}\right)\mathrm{d}x$$
$$= \hbar^2\frac{2}{a}\left(\frac{\pi}{a}\right)^2\left(\frac{a}{\pi}\right)\int_0^\pi \sin^2(u)\mathrm{d}u$$
$$= \hbar^2\frac{2\pi}{a^2}\left[\frac{x}{2} - \frac{\sin(2x)}{4}\right]\Bigg|_0^\pi$$
$$= \hbar^2\frac{2\pi}{a^2}\left[\frac{\pi}{2}\right] = \frac{\hbar^2\pi^2}{a^2} = \frac{h^2}{4a^2}$$

6. If $\widehat{A}$ is the operator corresponding to the mechanical quantity A and ϕ_n is an eigenfunction of $\widehat{A}$, such that

$$\widehat{A}\phi_n = a_n\phi_n$$

show that the expectation value of A is equal to a_n if the state of the system corresponds to ϕ_n. See Problem 5 for the formula for the expectation value.

$$\langle A\rangle = \frac{\int\phi_n^*\widehat{A}\phi_n\,\mathrm{d}x}{\int\phi_n^*\phi_n\,\mathrm{d}x} = \frac{\int\phi_n^* a_n\phi_n\,\mathrm{d}x}{\int\phi_n^*\phi_n\,\mathrm{d}x}$$
$$= \frac{a_n\int\phi_n^*\phi_n\,\mathrm{d}x}{\int\phi_n^*\phi_n\,\mathrm{d}x} = a_n$$

7. If x is an ordinary variable, the Maclaurin series for $1/(1-x)$ is

$$\frac{1}{1-x} = 1 + x^2 + x^3 + x^4 + \cdots.$$

If $\widehat{X}$ is some operator, show that the series

$$1 + \widehat{X} + \widehat{X}^2 + \widehat{X}^3 + \widehat{X}^4 + \cdots$$

is the inverse of the operator $1 - \widehat{X}$.

$$\left(1-\widehat{X}\right)\left(1 + \widehat{X} + \widehat{X}^2 + \widehat{X}^3 + \widehat{X}^4 + \cdots\right)$$
$$= 1 + \widehat{X} + \widehat{X}^2 + \widehat{X}^3 + \widehat{X}^4 + \cdots$$
$$-\left(\widehat{X} + \widehat{X}^2 + \widehat{X}^3 + \widehat{X}^4 + \cdots\right) = 1$$

8. Find the result of each operation on the given point (represented by Cartesian coordinates):

a. $\widehat{i}(2,4,6) = (-2,-4,-6)$
b. $\widehat{C}_{2(y)}(1,1,1) = (-1,1,-1)$

9. Find the result of each operation on the given point (represented by Cartesian coordinates):

a. $\widehat{C}_{3(z)}(1,1,1) = \left(-\frac{1}{2},\frac{1}{2}\sqrt{3}.1\right)$
b. $\widehat{S}_{4(z)}(1,1,1) = (1,-1,-1)$

10. Find the result of each operation on the given point (represented by Cartesian coordinates):

a. $\widehat{C}_{2(z)}\hat{\imath}\hat{\sigma}_h(1,1,1) = \widehat{C}_2(z)\hat{\imath}(-1,-1,1)$
$= \widehat{C}_2(z)(1,1,-1) = (1,-1,-1)$
b. $\widehat{S}_{2(y)}\hat{\sigma}_h(1,1,0) = \hat{S}_{2(y)}(1,1,0) = (-1,1,0)$

11. Find the result of each operation on the given point (represented by Cartesian coordinates):

a. $\widehat{C}_{2(z)}\hat{\imath}(1,1,1) = \widehat{C}_{2(z)}(-1,-1,-1)$
$= (1,-1,-1)$
b. $\hat{\imath}\widehat{C}_{2(z)}(1,1,1) = \hat{\imath}(-1,-1,1) = (1,1,-1)$

12. Find the 3 by 3 matrix that is equivalent in its action to each of the symmetry operators:

a. $\widehat{S}_{2(z)}$

$$x' = -x$$
$$y' = -y$$
$$z' = -z$$

$$\widehat{S}_2(z) \leftrightarrow \begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix}$$

b. $\widehat{C}_2(x)$

$$x' = x$$
$$y' = -y$$
$$z' = -z$$

$$\widehat{S}_2(z) \leftrightarrow \begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix}$$

13. Find the 3 by 3 matrix that is equivalent in its action to each of the symmetry operators:

a. $\widehat{C}_8(x)$: Let $\alpha = \pi/8 \leftrightarrow 45°$

$$x' = x$$
$$y' = \cos(\alpha)y + \sin(\alpha)z = \frac{1}{\sqrt{2}}(y+z)$$
$$z' = \sin(\alpha)y + \cos(\alpha)z = \frac{1}{\sqrt{2}}(y+z)$$

$$\widehat{C}_8(x) \leftrightarrow \begin{matrix} 1 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} \end{matrix}$$

b. $\widehat{S}_6(x)$: Let $\alpha = \pi/3 \leftrightarrow 60°$

$$x' = \cos(\alpha)x - \sin(\alpha)y = \frac{1}{2}x - \frac{\sqrt{3}}{2}y$$
$$y' = \sin(\alpha)x + \cos(\alpha)y = \frac{\sqrt{3}}{2}x + \frac{1}{2}y$$
$$z' = -z.$$

$$\widehat{C}_8(x) \leftrightarrow \begin{matrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{matrix}$$

14. Give the function that results if the given symmetry operator operates on the given function for each of the following:

a. $\widehat{C}_4(z)x^2 = y^2$
b. $\hat{\sigma}_h x \cos(x/y) = x\cos(x/y)$

15. Give the function that results if the given symmetry operator operates on the given function for each of the following:

a. $\hat{\imath}(x+y+z^2) = (-x-y+z^2)$
b. $\widehat{S}_{4(x)}(x+y+z) = x+z-y$

16. Find the matrix products. Use Mathematica to check your result.

a. $$\begin{bmatrix} 0 & 1 & 2 \\ 4 & 3 & 2 \\ 7 & 6 & 1 \end{bmatrix}\begin{bmatrix} 1 & 2 & 3 \\ 6 & 8 & 1 \\ 7 & 4 & 3 \end{bmatrix} = \begin{bmatrix} 20 & 16 & 7 \\ 36 & 40 & 21 \\ 50 & 66 & 30 \end{bmatrix}$$

b. $$\begin{bmatrix} 6 & 3 & 2 & -1 \\ -7 & 4 & 3 & 2 \\ 1 & 3 & 2 & -2 \\ 6 & 7 & -1 & -3 \end{bmatrix}\begin{bmatrix} 4 & 7 & -6 & -8 \\ 3 & -6 & 8 & -6 \\ 2 & 3 & -3 & 4 \\ -1 & 4 & 2 & 3 \end{bmatrix} = \begin{bmatrix} 38 & 26 & -20 & -61 \\ -12 & -56 & 69 & 50 \\ 19 & -13 & 8 & -24 \\ 46 & -15 & 17 & -103 \end{bmatrix}$$

17. Find the matrix products. Use Mathematica to check your result.

a. $$\begin{bmatrix} 3 & 2 & 1 & 4 \end{bmatrix}\begin{bmatrix} 1 & 2 & 3 \\ 0 & 3 & -4 \\ 1 & -2 & 1 \\ 3 & 1 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 2 & 3 \\ 0 & 3 & -4 \\ 1 & -2 & 1 \\ 3 & 1 & 0 \end{bmatrix}$$

b. $$\begin{bmatrix} 1 & 2 & 3 \\ 0 & 3 & -4 \\ 1 & -2 & 1 \\ 3 & 1 & 0 \end{bmatrix}\begin{bmatrix} 2 \\ 3 \\ 3 \end{bmatrix} = \begin{bmatrix} 17 \\ -3 \\ -1 \\ 9 \end{bmatrix}$$

c. $$\begin{bmatrix} 6 & 3 & -1 \\ 7 & 4 & -2 \end{bmatrix}\begin{bmatrix} 1 & 4 & -7 & 3 \\ 2 & 5 & 8 & -2 \\ 3 & 6 & -9 & 1 \end{bmatrix} = \begin{bmatrix} 9 & 33 & -9 & 11 \\ 9 & 36 & 1 & 11 \end{bmatrix}$$

18. Show that $(AB)C = A(BC)$ for the matrices:
$$A = \begin{bmatrix} 0 & 1 & 2 \\ 3 & 1 & -4 \\ 2 & 3 & 1 \end{bmatrix} \quad B = \begin{bmatrix} 3 & 1 & 4 \\ -2 & 0 & 1 \\ 3 & 2 & 1 \end{bmatrix}$$

$$C = \begin{bmatrix} 0 & 3 & 1 \\ -4 & 2 & 3 \\ 3 & 1 & -2 \end{bmatrix}$$

$$\mathbf{AB} = \begin{bmatrix} 0 & 1 & 2 \\ 3 & 1 & -4 \\ 2 & 3 & 1 \end{bmatrix} \begin{bmatrix} 3 & 1 & 4 \\ -2 & 0 & 1 \\ 3 & 2 & 1 \end{bmatrix} = \begin{bmatrix} 4 & 4 & 3 \\ -5 & -5 & 9 \\ 3 & 4 & 12 \end{bmatrix}$$

$$(\mathbf{AB})\mathbf{C} = \begin{bmatrix} 4 & 4 & 3 \\ -5 & -5 & 9 \\ 3 & 4 & 12 \end{bmatrix} \begin{bmatrix} 0 & 3 & 1 \\ -4 & 2 & 3 \\ 3 & 1 & -2 \end{bmatrix} = \begin{bmatrix} -7 & 23 & 10 \\ 47 & -16 & -38 \\ 20 & 29 & -9 \end{bmatrix}$$

$$\mathbf{BC} = \begin{bmatrix} 3 & 1 & 4 \\ -2 & 0 & 1 \\ 3 & 2 & 1 \end{bmatrix} \begin{bmatrix} 0 & 3 & 1 \\ -4 & 2 & 3 \\ 3 & 1 & -2 \end{bmatrix} = \begin{bmatrix} 8 & 15 & -2 \\ 3 & -5 & -4 \\ -5 & 14 & 7 \end{bmatrix}$$

$$\mathbf{A}(\mathbf{BC}) = \begin{bmatrix} 0 & 1 & 2 \\ 3 & 1 & -4 \\ 2 & 3 & 1 \end{bmatrix} \begin{bmatrix} 8 & 15 & -2 \\ 3 & -5 & -4 \\ -5 & 14 & 7 \end{bmatrix} = \begin{bmatrix} -7 & 23 & 10 \\ 47 & -16 & -38 \\ 20 & 29 & -9 \end{bmatrix}$$

19. Show that $A(B + C) = AB + AC$ for the example matrices in the previous problem.

$$\mathbf{B} + \mathbf{C} = \begin{bmatrix} 3 & 1 & 4 \\ -2 & 0 & 1 \\ 3 & 2 & 1 \end{bmatrix} + \begin{bmatrix} 0 & 3 & 1 \\ -4 & 2 & 3 \\ 3 & 1 & -2 \end{bmatrix} = \begin{bmatrix} 3 & 4 & 5 \\ -6 & 2 & 4 \\ 6 & 3 & -1 \end{bmatrix}$$

$$\mathbf{A}(\mathbf{B} + \mathbf{C}) = \begin{bmatrix} 0 & 1 & 2 \\ 3 & 1 & -4 \\ 2 & 3 & 1 \end{bmatrix} \begin{bmatrix} 3 & 4 & 5 \\ -6 & 2 & 4 \\ 6 & 3 & -1 \end{bmatrix} = \begin{bmatrix} 6 & 8 & 2 \\ -21 & 2 & 23 \\ -6 & 17 & 21 \end{bmatrix}$$

$$\mathbf{AB} = \begin{bmatrix} 0 & 1 & 2 \\ 3 & 1 & -4 \\ 2 & 3 & 1 \end{bmatrix} \begin{bmatrix} 3 & 1 & 4 \\ -2 & 0 & 1 \\ 3 & 2 & 1 \end{bmatrix} = \begin{bmatrix} 4 & 4 & 3 \\ -5 & -5 & 9 \\ 3 & 4 & 12 \end{bmatrix}$$

$$\mathbf{AC} = \begin{bmatrix} 0 & 1 & 2 \\ 3 & 1 & -4 \\ 2 & 3 & 1 \end{bmatrix} \begin{bmatrix} 0 & 3 & 1 \\ -4 & 2 & 3 \\ 3 & 1 & -2 \end{bmatrix} = \begin{bmatrix} 2 & 4 & -1 \\ -16 & 7 & 14 \\ -9 & 13 & 9 \end{bmatrix}$$

$$\mathbf{AB} + \mathbf{AC} = \begin{bmatrix} 4 & 4 & 3 \\ -5 & -5 & 9 \\ 3 & 4 & 12 \end{bmatrix} + \begin{bmatrix} 2 & 4 & -1 \\ -16 & 7 & 14 \\ -9 & 13 & 9 \end{bmatrix} = \begin{bmatrix} 6 & 8 & 2 \\ -21 & 2 & 23 \\ -6 & 17 & 21 \end{bmatrix}$$

20. Test the following matrices for singularity. Find the inverses of any that are nonsingular. Multiply the original matrix by its inverse to check your work. Use Mathematica to check your work.

a. $\begin{bmatrix} 0 & 1 & 2 \\ 3 & 4 & 5 \\ 6 & 7 & 8 \end{bmatrix}$

$$\begin{vmatrix} 0 & 1 & 2 \\ 3 & 4 & 5 \\ 6 & 7 & 8 \end{vmatrix} = 0$$

Singular

b. $\begin{bmatrix} 6 & 8 & 1 \\ 7 & 3 & 2 \\ 4 & 6 & -9 \end{bmatrix}$

$$\begin{vmatrix} 6 & 8 & 1 \\ 7 & 3 & 2 \\ 4 & 6 & -9 \end{vmatrix} = 364$$

Not singular

$$\begin{bmatrix} 6 & 8 & 1 \\ 7 & 3 & 2 \\ 4 & 6 & -9 \end{bmatrix}^{-1} = \begin{bmatrix} -\frac{3}{28} & \frac{3}{14} & \frac{1}{28} \\ \frac{71}{364} & -\frac{29}{182} & -\frac{5}{364} \\ \frac{15}{182} & -\frac{1}{91} & -\frac{19}{182} \end{bmatrix}$$

Check:

$$\begin{bmatrix} 6 & 8 & 1 \\ 7 & 3 & 2 \\ 4 & 6 & -9 \end{bmatrix} \begin{bmatrix} -\frac{3}{28} & \frac{3}{14} & \frac{1}{28} \\ \frac{71}{364} & -\frac{29}{182} & -\frac{5}{364} \\ \frac{15}{182} & -\frac{1}{91} & -\frac{19}{182} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

21. Test the following matrices for singularity. Find the inverses of any that are nonsingular. Multiply the original matrix by its inverse to check your work. Use Mathematica to check your work.

a. $\begin{bmatrix} 3 & 2 & -1 \\ -4 & 6 & 3 \\ 7 & 2 & -1 \end{bmatrix}$

$$\begin{vmatrix} 3 & 2 & -1 \\ -4 & 6 & 3 \\ 7 & 2 & -1 \end{vmatrix} = 48$$

Not singular

$$\begin{bmatrix} 3 & 2 & -1 \\ -4 & 6 & 3 \\ 7 & 2 & -1 \end{bmatrix}^{-1} \begin{bmatrix} -\frac{1}{4} & 0 & \frac{1}{4} \\ \frac{17}{48} & \frac{1}{12} & -\frac{5}{48} \\ -\frac{25}{24} & \frac{1}{6} & \frac{13}{24} \end{bmatrix}$$

$$\begin{bmatrix} 3 & 2 & -1 \\ -4 & 6 & 3 \\ 7 & 2 & -1 \end{bmatrix} \begin{bmatrix} -\frac{1}{4} & 0 & \frac{1}{4} \\ \frac{17}{48} & \frac{1}{12} & -\frac{5}{48} \\ -\frac{25}{24} & \frac{1}{6} & \frac{13}{24} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

b. $\begin{bmatrix} 0 & 2 & 3 \\ 1 & 0 & 1 \\ 2 & 0 & 1 \end{bmatrix}$

$$\begin{vmatrix} 0 & 2 & 3 \\ 1 & 0 & 1 \\ 2 & 0 & 1 \end{vmatrix} = 2$$

Not singular

$$\begin{bmatrix} 0 & 2 & 3 \\ 1 & 0 & 1 \\ 2 & 0 & 1 \end{bmatrix}^{-1} = \begin{bmatrix} 0 & -1 & 1 \\ \frac{1}{2} & -3 & \frac{3}{2} \\ 0 & 2 & -1 \end{bmatrix}$$

Check:

$$\begin{bmatrix} 0 & 2 & 3 \\ 1 & 0 & 1 \\ 2 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & -1 & 1 \\ \frac{1}{2} & -3 & \frac{3}{2} \\ 0 & 2 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

22. Find the matrix P that results from the similarity transformation

$$\mathbf{P} = \mathbf{X}^{-1}\mathbf{Q}\mathbf{X},$$

where

$$\mathbf{Q} = \begin{bmatrix} 1 & 2 \\ 2 & 1 \end{bmatrix}, \mathbf{X} = \begin{bmatrix} 2 & 3 \\ 4 & 3 \end{bmatrix}.$$

$$\mathbf{X}^{-1} = \begin{bmatrix} 2 & 3 \\ 4 & 3 \end{bmatrix}^{-1} = \begin{bmatrix} -\frac{1}{2} & \frac{1}{2} \\ \frac{2}{3} & -\frac{1}{3} \end{bmatrix}$$

$$\mathbf{QX} = \begin{bmatrix} 1 & 2 \\ 2 & 1 \end{bmatrix} \begin{bmatrix} 2 & 3 \\ 4 & 3 \end{bmatrix} = \begin{bmatrix} 10 & 9 \\ 8 & 9 \end{bmatrix}$$

$$\mathbf{X}^{-1}\mathbf{QX} = \begin{bmatrix} -\frac{1}{2} & \frac{1}{2} \\ \frac{2}{3} & -\frac{1}{3} \end{bmatrix} \begin{bmatrix} 10 & 9 \\ 8 & 9 \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 4 & 3 \end{bmatrix}$$

23. The H_2O molecule belongs to the point group C_{2v}, which contains the symmetry operators $\widehat{E}$, $\widehat{C}_2$, $\hat{\sigma}_a$, and $\hat{\sigma}_b$, where the C_2 axis passes through the oxygen nucleus and midway between the two hydrogen nuclei, and where the σ_a mirror plane contains the three nuclei and the σ_b mirror plane is perpendicular to the σ_a mirror plane.

a. Find the 3 by 3 matrix that is equivalent to each symmetry operator.

$$\widehat{E} \leftrightarrow \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\widehat{C}_2 \leftrightarrow \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\hat{\sigma}_a \leftrightarrow \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\hat{\sigma}_b \leftrightarrow \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

b. Show that the matrices obtained in part (a) have the same multiplication table as the symmetry operators, and that they form a group. The multiplication table for the group was to be obtained in an exercise. The multiplication table is

	$\widehat{E}$	$\widehat{C}_2$	$\widehat{\sigma}_{v(yz)}$	$\widehat{\sigma}_{v(xz)}$
$\widehat{E}$	$\widehat{E}$	$\widehat{C}_2$	$\widehat{\sigma}_{v(yz)}$	$\widehat{\sigma}_{v(xz)}$
$\widehat{C}_2$	$\widehat{C}_2$	$\widehat{E}$	$\widehat{\sigma}_{v(xz)}$	$\widehat{\sigma}_{v(yz)}$
$\widehat{\sigma}_{v(yz)}$	$\widehat{\sigma}_{v(yz)}$	$\widehat{\sigma}_{v(xz)}$	$\widehat{E}$	$\widehat{C}_2$
$\widehat{\sigma}_{v(xz)}$	$\widehat{\sigma}_{v(xz)}$	$\widehat{\sigma}_{v(yz)}$	$\widehat{C}_2$	$\widehat{E}$

where $\widehat{\sigma}_{v(yz)} = \hat{\sigma}_a$ and $\widehat{\sigma}_{v(xz)} = \hat{\sigma}_b$. We perform a few of the multiplications.

$$\hat{\sigma}_a\hat{\sigma}_b \leftrightarrow \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \leftrightarrow \widehat{C}_2$$

$$\left(\widehat{C}_2\right)^2 \leftrightarrow \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \leftrightarrow \widehat{E}$$

$$\widehat{C}_2\widehat{\sigma}_{v(xz)} \leftrightarrow \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \leftrightarrow \widehat{\sigma}_{v(yz)}$$

24. The BF_3 molecule is planar with bond angles of 120°.

a. List the symmetry operators that belong to this molecule. We place the molecule in the x-y plane with the boron atom at the origin and one of the fluorine atoms on the x axis. Call the fluorine atoms a, b, and c starting at the x axis and proceeding counterclockwise around the x-y plane. The symmetry elements are: a threefold rotation axis, three vertical mirror planes containing a fluorine atom, the horizontal mirror plane, and three twofold rotation axes containing a fluorine atom. The operators are $\widehat{E},\widehat{C}_{3(z)},\widehat{\sigma}_a,\widehat{\sigma}_b,\widehat{\sigma}_c,\widehat{\sigma}_h,\widehat{C}_{2a},\widehat{C}_{2b},\widehat{C}_{2c}$.

b. Find the three-dimensional matrices corresponding to the operators:

i. $\widehat{C}_{3(z)}$

$$\begin{aligned} x' &= \cos(120°)x - \sin(120°)y \\ &= -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ y' &= \sin(120°)x + \cos(120°)y \\ &= \frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z' &= z. \end{aligned}$$

$$\widehat{C}_3(z) \leftrightarrow \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

ii. $\widehat{\sigma}_a$

$$\begin{aligned} x' &= x \\ y' &= -y \\ z' &= z \end{aligned}$$

$$\widehat{\sigma}_a \leftrightarrow \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

iii. $\widehat{C}_{2a}$

$$\begin{aligned} x' &= x \\ y' &= -y \\ z' &= z \end{aligned}$$

$$\widehat{C}_{2a} \leftrightarrow \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

c. Find the following operator products:

i. $\widehat{C}_{3(z)}\widehat{\sigma}_a = \widehat{\sigma}_c$
ii. $\widehat{\sigma}_a\widehat{\sigma}_h = \widehat{\sigma}_a$
iii. $\widehat{C}_{3(z)}\widehat{C}_{2a} = \widehat{\sigma}_c$

The Solution of Simultaneous Algebraic Equations with More Than Two Unknowns

EXERCISES

Exercise 14.1. Use the rules of matrix multiplication to show that Eq. (14.3) is identical with Eqs. (14.1) and (14.2).

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} c_1 \\ \\ \\ c_2 \end{bmatrix}$$

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 &= c_1 \\ a_{21}x_1 + a_{22}x_2 &= c_2 \end{aligned}$$

Exercise 14.2. Use Cramer's rule to solve the simultaneous equations

$$\begin{aligned} 4x + 3y &= 17 \\ 2x - 3y &= -5 \end{aligned}$$

$$x = \frac{\begin{vmatrix} 17 & 3 \\ -5 & -3 \end{vmatrix}}{\begin{vmatrix} 4 & 3 \\ 2 & -3 \end{vmatrix}} = \frac{-51+15}{-12-6} = \frac{36}{18} = 2$$

$$y = \frac{\begin{vmatrix} 4 & 17 \\ 2 & -5 \end{vmatrix}}{\begin{vmatrix} 4 & 3 \\ 2 & -3 \end{vmatrix}} = \frac{-20-34}{-12-6} = \frac{54}{18} = 3$$

Exercise 14.3. Find the values of x_2 and x_3 for the previous example.

$$x_2 = \frac{\begin{vmatrix} 2 & 21 & 1 \\ 1 & 4 & 1 \\ 1 & 10 & 1 \end{vmatrix}}{\begin{vmatrix} 2 & 4 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & 1 \end{vmatrix}} = \frac{2\begin{vmatrix} 4 & 1 \\ 10 & 1 \end{vmatrix} - 21\begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix} + 1\begin{vmatrix} 1 & 4 \\ 1 & 10 \end{vmatrix}}{2\begin{vmatrix} -1 & 1 \\ 1 & 1 \end{vmatrix} - 1\begin{vmatrix} 4 &] \\ 1 & 1 \end{vmatrix} + 1\begin{vmatrix} 4 &] \\ -1 & 1 \end{vmatrix}}$$

$$= \frac{2(4-10) - 21(0) + 10 - 4}{2(-1-1) - (4-1) + (4+1)} = \frac{-6}{-2} = 3$$

$$x_3 = \frac{\begin{vmatrix} 2 & 4 & 21 \\ 1 & -1 & 4 \\ 1 & 1 & 10 \end{vmatrix}}{\begin{vmatrix} 2 & 4 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & 1 \end{vmatrix}} = \frac{2\begin{vmatrix} -1 & 4 \\ 1 & 10 \end{vmatrix} - 1\begin{vmatrix} 4 & 21 \\ 1 & 10 \end{vmatrix} + 1\begin{vmatrix} 4 & 21 \\ -1 & 4 \end{vmatrix}}{2\begin{vmatrix} -1 & 1 \\ 1 & 1 \end{vmatrix} - 1\begin{vmatrix} 4 &] \\ 1 & 1 \end{vmatrix} + 1\begin{vmatrix} 4 &] \\ -1 & 1 \end{vmatrix}}$$

$$= \frac{2(-10-4) - 1(40-21) + 1(16+21)}{2(-1-1) - (4-1) + (4+1)}$$

$$= \frac{-10}{-2} = 5$$

Exercise 14.4. Find the value of x_1 that satisfies the set of equations

$$\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & 1 \\ 1 & 1 & -1 & 1 \\ 1 & 1 & 1 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} 10 \\ 6 \\ 4 \\ 1 \end{bmatrix}$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00014-8

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & 1 \\ 1 & 1 & -1 & 1 \\ 1 & 1 & 1 & -1 \end{vmatrix} = -8$$

$$\begin{vmatrix} 10 & 1 & 1 & 1 \\ 6 & -1 & 1 & 1 \\ 4 & 1 & -1 & 1 \\ 1 & 1 & 1 & -1 \end{vmatrix} = -4$$

$$x_1 = \frac{-4}{-8} = \frac{1}{2}$$

The complete solution is

$$\mathbf{X} = \begin{bmatrix} \frac{1}{2} \\ 2 \\ 3 \\ \frac{9}{2} \end{bmatrix}$$

Exercise 14.5. Determine whether the set of four equations in three unknowns can be solved:

$$\begin{aligned} x_1 + x_2 + x_3 &= 12 \\ 4x_1 + 2x_2 + 8x_3 &= 52 \\ 3x_1 + 3x_2 + x_3 &= 25 \\ 2x_1 + x_2 + 4x_3 &= 26 \end{aligned}$$

We first disregard the first equation. The determinant of the coefficients of the last three equations vanishes:

$$\begin{vmatrix} 4 & 2 & 8 \\ 3 & 3 & 1 \\ 2 & 1 & 4 \end{vmatrix} = 0$$

These three equations are apparently linearly dependent. We disregard the fourth equation and solve the first three equations. The result is:

$$x_1 = -\frac{5}{2}, \quad x_2 = 9, \quad x_3 = \frac{11}{2}$$

Exercise 14.6. Solve the simultaneous equations by matrix inversion

$$\begin{aligned} 2x_1 + x_2 &= 4 \\ x_1 + 2x_2 + x_3 &= 7 \\ x_2 + 2x_3 &= 8 \end{aligned}$$

$$\begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix}^{-1} = \begin{bmatrix} \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \\ \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{bmatrix}$$

$$\begin{bmatrix} \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \\ \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{bmatrix} \begin{bmatrix} 4 \\ 7 \\ 8 \end{bmatrix} = \begin{bmatrix} \frac{3}{2} \\ 1 \\ \frac{7}{2} \end{bmatrix}$$

The solution is

$$x_1 = \frac{3}{2}, \quad x_2 = 1, \quad x_3 = \frac{7}{2}$$

Exercise 14.7. Use Gauss–Jordan elimination to solve the set of simultaneous equations in the previous exercise. The same row operations will be required that were used in Example 13.16.

$$\begin{aligned} 2x_1 + x_2 &= 1 \\ x_1 + 2x_2 + x_3 &= 2 \\ x_2 + 2x_3 &= 3 \end{aligned}$$

In matrix notation

$$\mathbf{AX} = \mathbf{C}$$

$$\begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$$

The augmented matrix is

$$\begin{bmatrix} 2 & 1 & 0 & \vdots & 1 \\ 1 & 2 & 1 & \vdots & 2 \\ 0 & 1 & 2 & \vdots & 3 \end{bmatrix}$$

We multiply the first row by $\frac{1}{2}$, obtaining

$$\begin{bmatrix} 1 & \frac{1}{2} & 0 & \vdots & \frac{1}{2} \\ 1 & 2 & 1 & \vdots & 2 \\ 0 & 1 & 2 & \vdots & 3 \end{bmatrix}.$$

We subtract the first row from the second and replace the second row by this difference. The result is

$$\begin{bmatrix} 1 & \frac{1}{2} & 0 & \vdots & \frac{1}{2} \\ 0 & \frac{3}{2} & 1 & \vdots & \frac{3}{2} \\ 0 & 1 & 2 & \vdots & 3 \end{bmatrix}.$$

We multiply the second row by $\frac{1}{3}$

$$\begin{bmatrix} 1 & \frac{1}{2} & 0 & \vdots & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{3} & \vdots & \frac{1}{2} \\ 0 & 1 & 2 & \vdots & 3 \end{bmatrix}.$$

We replace the first row by the difference of the first row and the second to obtain

$$\begin{bmatrix} 1 & 0 & -\frac{1}{3} & \vdots & 0 \\ 0 & \frac{1}{2} & \frac{1}{3} & \vdots & \frac{1}{2} \\ 0 & 1 & 2 & \vdots & 3 \end{bmatrix}.$$

We multiply the second row by 2,

$$\begin{bmatrix} 1 & 0 & -\frac{1}{3} & \vdots & 0 \\ 0 & 1 & \frac{2}{3} & \vdots & 1 \\ 0 & 1 & 2 & \vdots & 3 \end{bmatrix}.$$

We subtract the second row from the third row, and replace the third row by the difference. The result is

$$\begin{bmatrix} 1 & 0 & -\frac{1}{3} & \vdots & 0 \\ 0 & 1 & \frac{2}{3} & \vdots & 1 \\ 0 & 0 & \frac{4}{3} & \vdots & 2 \end{bmatrix}.$$

We now multiply the third row by $\frac{1}{2}$,

$$\begin{bmatrix} 1 & 0 & -\frac{1}{3} & \vdots & 0 \\ 0 & 1 & \frac{2}{3} & \vdots & 1 \\ 0 & 0 & \frac{2}{3} & \vdots & 1 \end{bmatrix}.$$

We subtract the third row from the second and replace the second row by the difference, obtaining

$$\begin{bmatrix} 1 & 0 & -\frac{1}{3} & \vdots & 0 \\ 0 & 1 & 0 & \vdots & 0 \\ 0 & 0 & \frac{2}{3} & \vdots & 1 \end{bmatrix}.$$

We now multiply the third row by $\frac{1}{2}$,

$$\begin{bmatrix} 1 & 0 & -\frac{1}{3} & \vdots & \frac{1}{2} \\ 0 & 1 & 0 & \vdots & 0 \\ 0 & 0 & \frac{1}{3} & \vdots & \frac{1}{2} \end{bmatrix}$$

We add the third row to the first row, and replace the first row by the sum. The result is

$$\begin{bmatrix} 1 & 0 & 0 & \vdots & \frac{1}{2} \\ 0 & 1 & 0 & \vdots & 0 \\ 0 & 0 & \frac{1}{3} & \vdots & \frac{1}{2} \end{bmatrix}.$$

We multiply of the third row by 3 to obtain

$$\begin{bmatrix} 1 & 0 & 0 & \vdots & \frac{1}{2} \\ 0 & 1 & 0 & \vdots & 0 \\ 0 & 0 & 1 & \vdots & \frac{3}{2} \end{bmatrix}.$$

We now reconstitute the matrix equation. The left-hand side of the equation is **EX** and the right-hand side of the equation is equal to **X**.

$$\mathbf{AX} = \mathbf{C}$$

$$\mathbf{EX} = \mathbf{C}' = \mathbf{X}$$

$$\mathbf{EX} = \mathbf{X} = \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{3}{2} \end{bmatrix}.$$

The solution is

$$x_1 = \frac{1}{2}, \quad x_2 = 0, \quad x_3 = \frac{3}{2}$$

Exercise 14.8. Find expressions for x and y in terms of z for the set of equations

$$\begin{aligned} 2x + 3y - 12z &= 0 \\ x - y - z &= 0 \\ 3x + 2y - 13z &= 0 \end{aligned}$$

The determinant of the coefficients is

$$\begin{vmatrix} 2 & 3 & -12 \\ 1 & -1 & -1 \\ 3 & 2 & -13 \end{vmatrix} = 0$$

Since the determinant vanishes, this system of equations can have a nontrivial solution. We multiply the second equation by 3 and add the first two equations:

$$\begin{aligned} 5x - 15z &= 0 \\ x &= 3z \end{aligned}$$

We multiply the second equation by 2 and subtract the second equation from the first:

$$\begin{aligned} 5y - 10z &= 0 \\ y &= 2z \end{aligned}$$

Exercise 14.9. Show that the second eigenvector in the previous example is an eigenvector.

$$\begin{bmatrix} \sqrt{2} & 1 & 0 \\ 1 & \sqrt{2} & 1 \\ 0 & 1 & \sqrt{2} \end{bmatrix} \begin{bmatrix} 1/2 \\ -1/\sqrt{2} \\ 1/2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

Exercise 14.10. Find the third eigenvector for the previous example.

$$\begin{aligned} -\sqrt{2}x_1 + x_2 + 0 &= 0 \\ x_1 - \sqrt{2}x_2 + x_3 &= 0 \\ 0 + x_2 - \sqrt{2}x_3 &= 0 \end{aligned}$$

The solution is:

$$x_1 = x_3, \quad x_2 = x_3\sqrt{2}$$

With the normalization condition

$$x_3^2 + 2x_3^2 + x_3^2 = 4x_3^2$$

$$\begin{aligned} x_1 &= x_3 = \frac{1}{2} \\ x_2 &= \frac{\sqrt{2}}{2} = \sqrt{\frac{1}{2}} \end{aligned}$$

$$\mathbf{X} = \begin{bmatrix} 1/2 \\ 1/\sqrt{2} \\ 1/2 \end{bmatrix}$$

Exercise 14.11. The Hückel secular equation for the hydrogen molecule is

$$\begin{vmatrix} \alpha - W & \beta \\ \beta & \alpha - W \end{vmatrix} = 0$$

Determine the two orbital energies in terms of α and β.

$$\begin{matrix} x & 1 \\ 1 & x \end{matrix} = 0 = x^2 - 1$$

$$x = \pm 1$$

$$W = \begin{cases} \alpha - \beta \\ \alpha + \beta \end{cases}$$

PROBLEMS

1. Solve the set of simultaneous equations:

$$\begin{aligned} 3x + y + 2z &= 17 \\ x - 3y + z &= -3 \\ x + 2y - 3z &= -4 \end{aligned}$$

Find the inverse matrix

$$\begin{bmatrix} 3 & 1 & 2 \\ 1 & -3 & 1 \\ 1 & 2 & -3 \end{bmatrix}^{-1} = \begin{bmatrix} \frac{1}{5} & \frac{1}{5} & \frac{1}{5} \\ \frac{4}{35} & -\frac{11}{35} & -\frac{1}{35} \\ \frac{1}{7} & -\frac{1}{7} & -\frac{2}{7} \end{bmatrix}$$

:

$$\begin{bmatrix} \frac{1}{5} & \frac{1}{5} & \frac{1}{5} \\ \frac{4}{35} & -\frac{11}{35} & -\frac{1}{35} \\ \frac{1}{7} & -\frac{1}{7} & -\frac{2}{7} \end{bmatrix} \begin{bmatrix} 17 \\ -3 \\ -4 \end{bmatrix} = \begin{bmatrix} 2 \\ 3 \\ 4 \end{bmatrix}$$

$$x = 2, \quad y = 3, \quad z = 4$$

:

2. Solve the set of simultaneous equations

$$\begin{aligned} y + z &= 2 \\ x + z &= 3 \\ x + y &= 4 \end{aligned}$$

Find the inverse matrix:

$$\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}^{-1} = \begin{bmatrix} -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \end{bmatrix}$$

$$\begin{bmatrix} -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \end{bmatrix} \begin{matrix} 2 \\ 3 \\ 4 \end{matrix} = \begin{matrix} \frac{5}{2} \\ \frac{3}{2} \\ \frac{1}{2} \end{matrix}$$

$$x = \frac{5}{2}, \quad y = \frac{3}{2}, \quad z = \frac{1}{2}$$

3. Solve the set of equations, using Cramer's rule:

$$\begin{aligned} 3x_1 + x_2 + x_3 &= 19 \\ x_1 - 2x_2 + 3x_3 &= 13 \\ x_1 + 2x_2 + 2x_3 &= 23 \end{aligned}$$

$$x_1 = \frac{\begin{vmatrix} 19 & 1 & 1 \\ 13 & -2 & 3 \\ 23 & 2 & 2 \end{vmatrix}}{\begin{vmatrix} 3 & 1 & 1 \\ 1 & -2 & 3 \\ 1 & 2 & 2 \end{vmatrix}} = \frac{-75}{-25} = 3$$

$$x_2 = \frac{\begin{vmatrix} 3 & 19 & 1 \\ 1 & 13 & 3 \\ 1 & 23 & 2 \end{vmatrix}}{\begin{vmatrix} 3 & 1 & 1 \\ 1 & -2 & 3 \\ 1 & 2 & 2 \end{vmatrix}} = \frac{-100}{-25} = 4$$

$$x_3 = \frac{\begin{vmatrix} 3 & 1 & 19 \\ 1 & -2 & 13 \\ 1 & 2 & 23 \end{vmatrix}}{\begin{vmatrix} 3 & 1 & 1 \\ 1 & -2 & 3 \\ 1 & 2 & 2 \end{vmatrix}} = \frac{-150}{-25} = 6$$

Verify your result using Mathematica.

$$\begin{bmatrix} 3 & 1 & 1 \\ 1 & -2 & 3 \\ 1 & 2 & 2 \end{bmatrix}^{-1} = \begin{bmatrix} \frac{2}{5} & 0 & -\frac{1}{5} \\ -\frac{1}{25} & -\frac{1}{5} & \frac{8}{25} \\ -\frac{4}{25} & \frac{1}{5} & \frac{7}{25} \end{bmatrix}$$

$$\begin{bmatrix} \frac{2}{5} & 0 & -\frac{1}{5} \\ -\frac{1}{25} & -\frac{1}{5} & \frac{8}{25} \\ -\frac{4}{25} & \frac{1}{5} & \frac{7}{25} \end{bmatrix} \begin{bmatrix} 19 \\ 13 \\ 23 \end{bmatrix} = \begin{bmatrix} 3 \\ 4 \\ 6 \end{bmatrix}$$

4. Solve the set of equations, using Gauss-Jordan elimination.

$$\begin{aligned} x_1 + x_2 &= 6 \\ 2x_2 - x_3 &= 1 \\ x_1 + 2x_2 &= 5 \end{aligned}$$

Write the augmented matrix

$$\left[\begin{array}{ccc:c} 1 & 1 & 0 & 6 \\ 0 & 2 & -1 & 1 \\ 1 & 2 & 0 & 5 \end{array}\right]$$

Multiply the first row by 2

$$\left[\begin{array}{ccc:c} 2 & 2 & 0 & 12 \\ 0 & 2 & -1 & 1 \\ 1 & 2 & 0 & 5 \end{array}\right]$$

Subtract the third line from the first line and replace the first line by the difference

$$\left[\begin{array}{ccc:c} 1 & 0 & 0 & 7 \\ 0 & 2 & -1 & 1 \\ 1 & 2 & 0 & 5 \end{array}\right]$$

Subtract the second line from the third line and replace the third line by the difference

$$\left[\begin{array}{ccc:c} 1 & 0 & 0 & 7 \\ 0 & 2 & -1 & 1 \\ 1 & 0 & 1 & 4 \end{array}\right]$$

Subtract the third line from the first line and replace the third line by the difference

$$\left[\begin{array}{ccc:c} 1 & 0 & 0 & 7 \\ 0 & 2 & -1 & 1 \\ 0 & 0 & -1 & 3 \end{array}\right]$$

Subtract the third line from the second line and replace the second line by the difference

$$\left[\begin{array}{ccc:c} 1 & 0 & 0 & 7 \\ 0 & 2 & 0 & -2 \\ 0 & 0 & -1 & 3 \end{array}\right]$$

Multiply the second line by 1/2 and the second line by -1

$$\left[\begin{array}{ccc:c} 1 & 0 & 0 & 7 \\ 0 & 1 & 0 & -1 \\ 0 & 0 & 1 & -3 \end{array}\right]$$

The solution is

$$x_1 = 7, \quad x_2 = -1, \quad x_3 = -3$$

Use Mathematica to confirm your solution.

$$\begin{bmatrix} 1 & 1 & 0 \\ 0 & 2 & -1 \\ 1 & 2 & 0 \end{bmatrix}^{-1} = \begin{bmatrix} 2 & 0 & -1 \\ -1 & 0 & 1 \\ -2 & -1 & 2 \end{bmatrix}$$

$$\begin{bmatrix} 2 & 0 & -1 \\ -1 & 0 & 1 \\ -2 & -1 & 2 \end{bmatrix} \begin{bmatrix} 6 \\ 1 \\ 5 \end{bmatrix} = \begin{bmatrix} 7 \\ -1 \\ -3 \end{bmatrix}$$

$$x_1 = 7, \quad x_2 = -1, \quad x_3 = -3$$

5. Solve the equations:

$$\begin{aligned} 3x_1 + 4x_2 + 5x_3 &= 25 \\ 4x_1 + 3x_2 - 6x_3 &= -7 \\ x_1 + x_2 + x_3 &= 6 \end{aligned}$$

In matrix notation

$$\begin{bmatrix} 3 & 4 & 5 \\ 4 & 3 & -6 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} 25 \\ -7 \\ 6 \end{bmatrix}$$

The inverse matrix is

$$\begin{bmatrix} 3 & 4 & 5 \\ 4 & 3 & -6 \\ 1 & 1 & 1 \end{bmatrix}^{-1} = \begin{bmatrix} -\frac{9}{8} & -\frac{1}{8} & \frac{39}{8} \\ \frac{5}{4} & \frac{1}{4} & -\frac{19}{4} \\ -\frac{1}{8} & -\frac{1}{8} & \frac{7}{8} \end{bmatrix}$$

$$\begin{bmatrix} -\frac{9}{8} & -\frac{1}{8} & \frac{39}{8} \\ \frac{5}{4} & \frac{1}{4} & -\frac{19}{4} \\ -\frac{1}{8} & -\frac{1}{8} & \frac{7}{8} \end{bmatrix} \begin{bmatrix} 25 \\ -7 \\ 6 \end{bmatrix} = \begin{bmatrix} 2 \\ 1 \\ 3 \end{bmatrix}$$

The solution is

$$x_1 = 2, \quad x_2 = 1, \quad x_3 = 3$$

6. Solve the equation:

$$\begin{bmatrix} 1 & 1 & 1 & 3 \\ 2 & 1 & 1 & 1 \\ 1 & 2 & 3 & 4 \\ 2 & 0 & 1 & 4 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} 6 \\ 5 \\ 10 \\ 7 \end{bmatrix}.$$

The inverse matrix is

$$\begin{bmatrix} 1 & 1 & 1 & 3 \\ 2 & 1 & 1 & 1 \\ 1 & 2 & 3 & 4 \\ 2 & 0 & 1 & 4 \end{bmatrix}^{-1} = \begin{bmatrix} -\frac{1}{6} & \frac{1}{2} & -\frac{1}{6} & \frac{1}{6} \\ \frac{5}{4} & \frac{1}{4} & -\frac{1}{4} & -\frac{3}{4} \\ -\frac{4}{3} & 0 & \frac{2}{3} & \frac{1}{3} \\ \frac{5}{12} & -\frac{1}{4} & -\frac{1}{12} & \frac{1}{12} \end{bmatrix}$$

$$\begin{bmatrix} -\frac{1}{6} & \frac{1}{2} & -\frac{1}{6} & \frac{1}{6} \\ \frac{5}{4} & \frac{1}{4} & -\frac{1}{4} & -\frac{3}{4} \\ -\frac{4}{3} & 0 & \frac{2}{3} & \frac{1}{3} \\ \frac{5}{12} & -\frac{1}{4} & -\frac{1}{12} & \frac{1}{12} \end{bmatrix} \begin{bmatrix} 6 \\ 5 \\ 10 \\ 7 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}$$

The solution is

$$x_1 = x_2 = x_3 = x_4 = 1$$

7. Decide whether the following set of equations has a solution. Solve the equations if it does.

$$\begin{aligned} 3x + 4y + z &= 13 \\ 4x + 3y + 2z &= 10 \\ 7x + 7y + 3z &= 23 \end{aligned}$$

The determinant of the coefficients is

$$\begin{vmatrix} 3 & 4 & 1 \\ 4 & 3 & 2 \\ 7 & 7 & 3 \end{vmatrix} = 0$$

A solution of x and y in terms of z is possible. Solve the first two equations

$$\begin{bmatrix} 3 & 4 \\ 4 & 3 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} 13 - z \\ 10 - 2z \end{bmatrix}$$

Use Gauss-Jordan elimination. Construct the augmented matrix

$$\begin{bmatrix} 3 & 4 & \vdots & 13 - z \\ 4 & 3 & \vdots & 10 - 2z \end{bmatrix}$$

Multiply the first equation by 3 and the second equation by 4:

$$\begin{bmatrix} 9 & 12 & \vdots & 39 - 3z \\ 16 & 12 & \vdots & 40 - 8z \end{bmatrix}$$

Subtract the first line from the second line and replace the first line by the difference

$$\left[\begin{array}{cc:c} 7 & 0 & 1-5z \\ 16 & 12 & 40-8z \end{array}\right]$$

Multiply the first line by 16 and the second line by 7

$$\left[\begin{array}{cc:c} 112 & 0 & 16-80z \\ 112 & 84 & 280-56z \end{array}\right]$$

Subtract the first line from the second line and replace the second line by the difference

$$\left[\begin{array}{cc:c} 112 & 0 & 16-80z \\ 0 & 84 & 264+24z \end{array}\right]$$

Divide the first equation by 112 and the second equation by 84:

$$\left[\begin{array}{cc:c} 1 & 0 & \frac{16}{112}-\frac{80}{112}z \\ 0 & 1 & \frac{264}{84}+\frac{24}{84}z \end{array}\right]$$

$$\begin{aligned} x &= \frac{16}{112}-\frac{80}{112}z = \frac{1}{7}-\frac{5}{7}z \\ y &= \frac{264}{84}+\frac{24}{84}z = \frac{22}{7}+\frac{2}{7}z \end{aligned}$$

8. Solve the set of equations by matrix inversion. If available, use Mathematica to invert the matrix.

$$\begin{aligned} 2x_1+4x_2+x_3 &= 40 \\ x_1+6x_2+2x_3 &= 55 \\ 3x_1+x_2+x_3 &= 23 \end{aligned}$$

The inverse matrix is

$$\begin{bmatrix} 2 & 4 & 1 \\ 1 & 6 & 2 \\ 3 & 1 & 1 \end{bmatrix}^{-1} = \begin{bmatrix} \frac{4}{11} & -\frac{3}{11} & \frac{2}{11} \\ \frac{5}{11} & -\frac{1}{11} & -\frac{3}{11} \\ -\frac{17}{11} & \frac{10}{11} & \frac{8}{11} \end{bmatrix}$$

$$\begin{bmatrix} \frac{4}{11} & -\frac{3}{11} & \frac{2}{11} \\ \frac{5}{11} & -\frac{1}{11} & -\frac{3}{11} \\ -\frac{17}{11} & \frac{10}{11} & \frac{8}{11} \end{bmatrix} \begin{bmatrix} 40 \\ 55 \\ 23 \end{bmatrix} = \begin{bmatrix} \frac{41}{11} \\ \frac{76}{11} \\ \frac{54}{11} \end{bmatrix}$$

The solution is

$$x_1 = \frac{41}{11}, \quad x_2 = \frac{76}{11}, \quad x_3 = \frac{54}{11}$$

Check the inverse

$$\begin{bmatrix} 2 & 4 & 1 \\ 1 & 6 & 2 \\ 3 & 1 & 1 \end{bmatrix} \begin{bmatrix} \frac{4}{11} & -\frac{3}{11} & \frac{2}{11} \\ \frac{5}{11} & -\frac{1}{11} & -\frac{3}{11} \\ -\frac{17}{11} & \frac{10}{11} & \frac{8}{11} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

9. Find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$$

The eigenvalues are 0,3. The eigenvectors are, for eigenvalue 0:

$$\begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix}$$

Check the first eigenvalue:

$$\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

For the eigenvalue 3, the eigenvector is

$$\begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$

Check this

$$\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} 3 \\ 3 \\ 3 \end{bmatrix}$$

The eigenvalue is equal to 3.

10. Find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}$$

The eigenvalues are -1, -1, and 2, and the eigenvectors are:

$$\left\{ \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix}, \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix} \right\} \leftrightarrow -1, \quad \left\{ \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \right\} \leftrightarrow 2$$

Check the first case:

$$\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$$

11. Find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 1 & 0 & 1 \\ 1 & 0 & 1 \\ 1 & 0 & 1 \end{bmatrix}$$

Does this matrix have an inverse? The eigenvalues are 0 and 2. The eigenvectors are

$$\left\{ \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix} \right\} \leftrightarrow 0, \quad \left\{ \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \right\} \leftrightarrow 2$$

Check the last case:

$$\begin{bmatrix} 1 & 0 & 1 \\ 1 & 0 & 1 \\ 1 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} 2 \\ 2 \\ 2 \end{bmatrix} D$$

The determinant is

$$\begin{vmatrix} 1 & 0 & 1 \\ 1 & 0 & 1 \\ 1 & 0 & 1 \end{vmatrix} = 0$$

There is no inverse matrix.

12. In the Hückel treatment of the cyclopropenyl radical, the basis functions are the three $2p_z$ atomic orbitals, which we denote by f_1, f_2, and f_3.

$$\psi = c_1 f_1 + c_2 f_2 + c_3 f_3$$

The possible values of the orbital energy W are sought as a function of the c coefficients by solving the three simultaneous equations

$$\begin{aligned} xc_1 + c_2 + c_3 &= 0 \\ c_1 + xc_2 + c_3 &= 0 \\ c_1 + c_2 + xc_3 &= 0 \end{aligned}$$

where $x = \left(\alpha - W)/\beta\right)$ and where α and β are certain integrals whose values are to be determined later.

a. The determinant of the c coefficients must be set equal to zero in order for a nontrivial solution to exist. This is the secular equation. Solve the secular equation and obtain the orbital energies.

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0$$

$$\begin{aligned} \begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} &= x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 1 \\ 1 & x \end{vmatrix} + \begin{vmatrix} 1 & x \\ 1 & 1 \end{vmatrix} \\ &= x^3 - x - x + 1 + 1 - x = 0 \\ &= x^3 - 3x + 2 = 0 \end{aligned}$$

$$x^3 - 3x + 2 = 0$$

The roots to this equation are

$$x = -2, \quad x = 1, \quad x = 1$$

The orbital energies are

$$W = \begin{cases} \alpha - \beta \\ \alpha - \beta \\ \alpha + 2\beta \end{cases}$$

b. Solve the three simultaneous equations, once for each value of x. Since there are only two independent equations, express c_2 and c_3 in terms of c_1. For $x = -2$:

$$\begin{aligned} -2c_1 + c_2 + c_3 &= 0 \\ c_1 - 2c_2 + c_3 &= 0 \\ c_1 + c_2 - 2c_3 &= 0 \end{aligned}$$

The solution is:

$$c_1 = c_2 = c_3$$

For $x = 1$:

$$\begin{aligned} c_1 + c_2 + c_3 &= 0 \\ c_1 + c_2 + c_3 &= 0 \\ c_1 + c_2 + c_3 &= 0 \end{aligned}$$

The solution is:

$$c_1 = 0, \quad c_2 = -c_3$$

or

$$c_2 = 0, \quad c_1 = -c_3$$

or

$$c_3 = 0, \quad c_1 = -c_2$$

c. Impose the normalization condition

$$c_1^2 + c_2^2 + c_3^2 = 1$$

to find the values of the c coefficients for each value of W. For $x = 1, W = \alpha - \beta$

$$c_1 = 0, \quad c_2 = \frac{1}{\sqrt{2}}, \quad c_3 = -\frac{1}{\sqrt{2}}$$

For $x = -2, W = \alpha + 2\beta$:

$$c_1 = \frac{1}{\sqrt{3}}, \quad c_2 = \frac{1}{\sqrt{3}}, \quad c_3 = \frac{1}{\sqrt{3}}$$

d. Check your work by using Mathematica to find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{bmatrix}$$

Using the Scientific Workplace software, we find that the eigenvalues are:

$$x+2,\ x-1$$

The eigenvectors are:

$$\left\{\begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix} \leftrightarrow x-1, \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix}\right\} \leftrightarrow x-1,$$

$$\left\{\begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}\right\} \leftrightarrow x+2,$$

Check the last case:

$$\begin{bmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{bmatrix}\begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} x+2 \\ x+2 \\ x+2 \end{bmatrix}$$

Chapter 15

Probability, Statistics, and Experimental Errors

EXERCISES

Exercise 15.1. List as many sources of error as you can for some of the following measurements. Classify each one as systematic or random and estimate the magnitude of each source of error.

a. The measurement of the diameter of a copper wire using a micrometer caliper.

Systematic: faulty calibration of the caliper 0.1 mm
Random: parallax and other errors in reading the caliper 0.1 mm

b. The measurement of the mass of a silver chloride precipitate in a porcelain crucible using a digital balance.

Systematic: faulty calibration of the balance 1 mg
Random: impurities in the sample
lack of proper drying of the sample
air currents

c. The measurement of the resistance of an electrical heater using an electronic meter.

Systematic: faulty calibration of the meter 2 Ω
Random: parallax error and other error in reading the meter 1 Ω

d. The measurement of the time required for an automobile to travel the distance between two highway markers nominally 1 km apart, using a stopwatch.

Systematic: faulty calibration of the stopwatch 0.2 s
incorrect spacing of the markers 0.5 s
Random: reaction time difference in pressing the start and stop buttons 0.3 s

The reader should be able to find additional error sources.

Exercise 15.2. Calculate the probability that "heads" will come up 60 times if an unbiased coin is tossed 100 times.

$$
\begin{aligned}
\text{probability} &= \frac{100!}{60!40!}\left(\frac{1}{2}\right)^{100} \\
&= \frac{9.3326\times 10^{157}}{(8.32099\times 10^{81})(8.15915\times 10^{47})} \\
&\quad \times 7.8886\times 10^{-31} = 0.01084
\end{aligned}
$$

Exercise 15.3. Find the mean and the standard deviation for the distribution of "heads" coins in the case of 10 throws of an unbiased coin. Find the probability that a single toss will give a value within one standard deviation of the mean.

The probabilities are as follows:

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00039-2

no. of heads $= n$	binomial coefficient	probability $= p_n$
0	1	0.0009766
1	10	0.009766
2	45	0.043947
3	120	0.117192
4	210	0.205086
5	252	0.2461032
6	210	0.205086
7	120	0.117192
8	45	0.043947
9	10	0.009766
10	1	0.0009766

$$\langle n\rangle = \sum_{n=1}^{10} p_n n = 5.000$$
$$\langle n^2\rangle = \sum_{n=1}^{10} p_n n^2 = 27.501$$

$$\sigma_n^2 = \langle n^2\rangle - \langle n\rangle^2 = 27.501 - 25.000 = 2.501$$
$$\sigma_n = \sqrt{2.501} = 1.581$$

The probability that n lies within one standard deviation of the mean is

probability $= 0.205086 + 0.2461032 + 0.205086 = 0.656$

This is close to the rule of thumb that roughly two-thirds of the probability lies within one standard deviation of the mean.

Exercise 15.4. If x ranges from 0.00 to 10.00 and if $f(x) = cx^2$, find the value of c so that $f(x)$ is normalized. Find the mean value of x, the root-mean-square value of x and the standard deviation.

$$1 = c\int_{0.00}^{10.00} x^2\,\mathrm{d}x = c\frac{1}{3}x^3\Big|_{0.00}^{10.00} = \frac{c}{3}(1000.0)$$
$$c = \frac{3}{1000.0} = 0.003000$$

$$\langle x\rangle = c\int_{0.00}^{10.00} x^3\,\mathrm{d}x = c\frac{1}{4}x^4\Big|_{0.00}^{10.00}$$
$$= \frac{0.003000}{4}(10000) = 7.50$$
$$\langle x^2\rangle = c\int_{0.00}^{10.00} x^4\,\mathrm{d}x = c\frac{1}{5}x^5\Big|_{0.00}^{10.00}$$
$$= \frac{0.003000}{5}(100000) = 60.0$$
$$x_{\mathrm{rms}} = \langle x^2\rangle^{1/2} = (60.0)^{1/2} = 7.75$$

$$\sigma_x^2 = \langle x^2\rangle - \langle x\rangle^2 = 60.0 - (7.50)^2 = 3.75$$
$$\sigma_x = \sqrt{3.75} = 1.94$$

Exercise 15.5. Calculate the mean and standard deviation of the Gaussian distribution, showing that μ is the mean and that σ is the standard deviation.

$$\langle x\rangle = \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} xe^{-(x-\mu)^2/2\sigma^2}\,\mathrm{d}x$$
$$= \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} (y+\mu)e^{-y^2/2\sigma^2}\,\mathrm{d}x$$
$$= \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} ye^{-y^2/2\sigma^2}\,\mathrm{d}x$$
$$+\frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} \mu e^{-y^2/2\sigma^2}\,\mathrm{d}y = 0 + \mu = \mu$$
$$\langle x^2\rangle = \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} x^2e^{-(x-\mu)^2/2\sigma^2}\,\mathrm{d}x$$
$$= \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} (y+\mu)^2e^{-y^2/2\sigma^2}\,\mathrm{d}y$$
$$= \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} (y^2+2y+\mu^2)e^{-y^2/2\sigma^2}\,\mathrm{d}y$$
$$= \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} y^2e^{-y^2/2\sigma^2}\,\mathrm{d}y$$
$$+\frac{2}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} ye^{-y^2/2\sigma^2}\,\mathrm{d}y$$
$$+\frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} \mu^2e^{-y^2/2\sigma^2}\,\mathrm{d}y$$
$$= \frac{1}{\sqrt{2\pi}\sigma}\left(\frac{\sqrt{\pi}}{2}(2\sigma^2)^{3/2}\right) + 0 + \mu^2 = \sigma^2 + \mu^2$$
$$\sigma_x^2 = \langle x^2\rangle = \mu^2 = \sigma^2$$
$$\sigma_x = \sigma$$

Exercise 15.6. Show that the fraction of a population lying between $\mu - 1.96\sigma$ and $\mu + 1.96\sigma$ is equal to 0.950 for the Gaussian distribution.

$$\text{fraction} = \frac{1}{\sqrt{2\pi}\sigma}\int_{\mu-1.96\sigma}^{\mu+1.96\sigma} e^{-(x-\mu)^2/2\sigma^2}\,\mathrm{d}x$$
$$= \frac{1}{\sqrt{2\pi}\sigma}\int_{-1.96\sigma}^{1.96\sigma} e^{-y^2/2\sigma^2}\,\mathrm{d}y$$
$$= \frac{1}{\sqrt{2\pi}\sigma}\int_{0}^{1.96\sigma} e^{-y^2/2\sigma^2}\,\mathrm{d}y$$

Let $u = \frac{y}{\sqrt{2}\sigma}$

$$y = 1.96\sigma \leftrightarrow u = \frac{1.96\sigma}{\sqrt{2}\sigma} = 1.386$$

$$\text{fraction} = \frac{\sqrt{2}\sigma}{\sqrt{2\pi}\sigma}\int_0^{1.386} e^{-u^2}\,\mathrm{d}u$$
$$= \frac{1}{\sqrt{\pi}}\int_0^{1.386} e^{-u^2}\,\mathrm{d}u = \mathrm{erf}(1.386) = 0.950$$

Exercise 15.7. For the lowest-energy state of a particle in a box of length L, find the probability that the particle will be found between $L/4$ and $3L/4$. The probability is

$$\begin{aligned}
(\text{probability}) &= \frac{2}{L}\int_{0.2500L}^{0.7500L} \sin^2(\pi x/L)\mathrm{d}x \\
&= \left(\frac{2}{L}\right)\left(\frac{L}{\pi}\right)\int_{0.7854}^{2.3562} \sin^2(y)\mathrm{d}y \\
&= \frac{2}{\pi}\left[\frac{y}{2} - \frac{\sin(y)\cos(y)}{2}\right]_{0.7854}^{2.3562} \\
&= \frac{2}{\pi}\left[\frac{2.3562}{2} - \frac{\sin(2.3562)\cos(2.3562)}{2}\right. \\
&\quad \left. - \frac{0.7854}{2} + \frac{\sin(0.7854)\cos(0.7854)}{2}\right] \\
&= \frac{2}{\pi}(1.1781 + 0.2500 - 0.39270 + 0.2500) \\
&= 0.8183
\end{aligned}$$

Exercise 15.8. Find the expectation values for p_x and p_x^2 for our particle in a box in its lowest-energy state. Find the standard deviation.

$$\begin{aligned}
\langle p_x\rangle &= \frac{\hbar}{i}\frac{2}{L}\int_0^L \sin(\pi x/L)\left[\frac{\mathrm{d}}{\mathrm{d}x}\sin(\pi x/L)\right]\mathrm{d}x \\
&= \frac{\hbar}{i}\frac{2}{L}\frac{\pi}{L}\int_0^L \sin(\pi x/L)\cos(\pi x/L)\mathrm{d}x \\
&= \frac{\hbar}{i}\frac{2}{L}\frac{\pi}{L}\frac{L}{\pi}\int_0^{\pi} \sin(u)\cos(u)\mathrm{d}u \\
&= \frac{\hbar}{i}\frac{2}{L}\left.\frac{\sin^2(u)}{2}\right|_0^{\pi} = 0
\end{aligned}$$

This vanishing value of the momentum corresponds to the fact that the particle might be traveling in either direction with the same probability. The expectation value of the square of the momentum does not vanish:

$$\begin{aligned}
\langle p_x^2\rangle &= -\hbar^2\frac{2}{L}\int_0^L \sin(\pi x/L)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\sin(\pi x/L) \\
&= \left(\frac{\pi}{L}\right)^2\hbar^2\frac{2}{L}\int_0^L \sin^2(\pi x/L)\mathrm{d}x \\
&= \left(\frac{\pi}{L}\right)^2\hbar^2\frac{2}{L}\frac{L}{\pi}\int_0^{\pi} \sin^2(u)\mathrm{d}u \\
&= \left(\frac{\pi}{L}\right)^2\hbar^2\frac{2}{L}\frac{L}{\pi}\left[\frac{u}{2} - \frac{\sin(2u)}{4}\right]\Bigg|_0^{\pi} \\
&= \left(\frac{\pi}{L}\right)^2\hbar^2\frac{2}{L}\frac{L}{\pi}\frac{\pi}{2} = \frac{\pi^2\hbar^2}{L^2} = \frac{h^2}{4L^2}
\end{aligned}$$

$$\begin{aligned}
\sigma_{p_x}^2 &= \langle p_x^2\rangle - \langle p_x\rangle = \frac{h^2}{4L^2} \\
\sigma_{p_x} &= \frac{h}{2L}
\end{aligned}$$

Exercise 15.9. Find the expression for $\langle v_x^2\rangle^{1/2}$, the root-mean-square value of v_x, and the expression for the standard deviation of v_x.

$$\begin{aligned}
\langle v_x^2\rangle &= \left(\frac{m}{2\pi k_B T}\right)^{1/2}\int_{-\infty}^{\infty} v_x^2 \exp\left(-\frac{mv_x^2}{2k_BT}\right)\mathrm{d}v_x \\
&= 2\left(\frac{m}{2\pi k_B T}\right)^{1/2}\int_0^{\infty} v_x^2 \exp\left(-\frac{mv_x^2}{2k_BT}\right)\mathrm{d}v_x \\
&= 2\left(\frac{m}{2\pi k_B T}\right)^{1/2}\left(\frac{2k_BT}{m}\right)^{3/2}\int_0^{\infty} u^2 \\
&\quad \times \exp(-u^2)\,\mathrm{d}u \\
&= 2\left(\frac{m}{2\pi k_B T}\right)^{1/2}\left(\frac{2k_BT}{m}\right)^{3/2}\frac{\sqrt{\pi}}{4} = \frac{k_BT}{m}
\end{aligned}$$

$$\begin{aligned}
\sigma_{v_x}^2 &= \langle v_x^2\rangle - 0 = \langle v_x^2\rangle = \frac{k_BT}{m} \\
\sigma_{v_x} &= \sqrt{\frac{k_BT}{m}}
\end{aligned}$$

Exercise 15.10. Evaluate of $\langle v\rangle$ for N_2 gas at 298.15 K.

$$\begin{aligned}
\langle v\rangle &= \left(\frac{8RT}{\pi M}\right)^{1/2} \\
&= \left(\frac{8(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}{\pi(0.028013\ \mathrm{kg\ mol^{-1}})}\right)^{1/2} \\
&= 474.7\ \mathrm{m\ s^{-1}}
\end{aligned}$$

Exercise 15.11. Evaluate v_{rms} for N_2 gas at 298.15 K.

$$\begin{aligned}
v_{\mathrm{rms}} &= \left(\frac{3RT}{M}\right)^{1/2} \\
&= \left(\frac{3(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}{(0.028013\ \mathrm{kg\ mol^{-1}})}\right)^{1/2} \\
&= 515.2\ \mathrm{m\ s^{-1}}
\end{aligned}$$

Exercise 15.12. Evaluate the most probable speed for nitrogen molecules at 298.15 K.

$$\begin{aligned}
v_{mp} &= \left(\frac{2RT}{M}\right)^{1/2} \\
&= \left(\frac{2(8.3145\ \mathrm{J\ K^{-1}\ mol^{=1}})(298.15\ \mathrm{K})}{(0.028013\ \mathrm{kg\ mol^{-1}})}\right)^{1/2} \\
&= 420.7\ \mathrm{m\ s^{-1}}
\end{aligned}$$

Exercise 15.13. Find the value of the z coordinate after 1.00 s and find the time-average value of the z coordinate of the particle in the previous example for the first 1.00 s of fall if the initial position is $z = 0.00$ m.

$$\begin{aligned} z_z(t) - z(0) &= v_z(0)t - \frac{1}{2}gt^2 \\ &= -\frac{1}{2}(9.80 \text{ m s}^{-2})t^2 = -4.90 \text{ m} \end{aligned}$$

$$\begin{aligned} \overline{z} &= -\frac{1}{2(1.00 \text{ s})}\int_0^{1.00} gt^2 \, \mathrm{d}t \\ &= -\left(\frac{(9.80 \text{ m s}^{-2})}{2(1.00 \text{ s})}\right)\left[\frac{t^3}{3}\right]_0^{1.00} \\ &= -\left(\frac{9.80 \text{ m s}^{-2}}{2.00 \text{ s}}\right)\left(\frac{(1.00 \text{ s})^3}{3}\right) \\ &= -1.633 \text{ m} \end{aligned}$$

Exercise 15.14. A sample of 7 individuals has the following set of annual incomes: \$40000, \$41,000, \$41,000, \$62,000, \$65,000, \$125,000, and \$650,000. Find the mean income, the median income, and the mode of this sample.

$$\begin{aligned} \text{mean} &= \frac{1}{7}(\$40{,}000 + \$41{,}000 + \$41{,}000 + \$62{,}000 \\ &\quad + \$65{,}000 + \$125{,}000 + \$650{,}000) \\ &= \$146{,}300 \\ \text{median} &= \$62{,}000 \\ \text{mode} &= \$41{,}000 \end{aligned}$$

Notice how the presence of two high-income members of the set cause the mean to exceed the median. Some persons might try to mislead you by announcing a number as an "average" without specifying whether it is a median or a mean.

Exercise 15.15. Find the mean, $\langle x \rangle$, and the sample standard deviation, s_x, for the following set of values: $x = 2.876$ m, 2.881 m, 2.864 m, 2.879 m, 2.872 m, 2.889 m, 2.869 m. Determine how many values lie below $\langle x \rangle - s_x$ and how many lie above $\langle x \rangle + s_x$.

$$\begin{aligned} \langle x \rangle &= 2.876 \\ s_x^2 &= \frac{1}{6}[(0.000)^2 + (-0.005)^2 + (-0.012)^2 \\ &\quad + (0.003)^2 + (-0.004)^2 \\ &\quad + (0.013)^2 + (-0.007)^2] \\ &= 0.0000687 \\ s_x &= \sqrt{0.0000687} = 0.008 \end{aligned}$$

$$\langle x \rangle - s_x = 2.868, \langle x \rangle + s_x = 2.884$$

There is one value smaller than 2.868, and one value greater than 2.884. Five of the seven values, or 71%, lie in the range between $\langle x \rangle - s_x$ and $\langle x \rangle + s_x$.

Exercise 15.16. Assume that the H–O–H bond angles in various crystalline hydrates have been measured to be $108°, 109°, 110°, 103°, 111°$, and $107°$. Give your estimate of the correct bond angle and its 95% confidence interval.

$$\begin{aligned} \text{Bond angle} &= \langle \alpha \rangle = \frac{1}{6}(108° + 109° + 110° + 103° \\ &\quad + 111^{\circ} + 107°) = 108° \\ s &= 2.8° \\ \varepsilon &= \frac{(2.571)(2.8°)}{\sqrt{6}} = 3.3° \end{aligned}$$

Exercise 15.17. Apply the Q test to the 39.75 °C data point appended to the data set of the previous example.

$$\begin{aligned} Q &= \frac{|(\text{outlying value}) - (\text{value nearest the outlying value})|}{(\text{highest value}) - (\text{lowest value})} \\ &= \frac{42.58 - 39.75}{42.83 - 39.75} = \frac{2.83}{3.08} = 0.919 \end{aligned}$$

By interpolation in Table 15.2 for $N = 11$, the critical Q value is 0.46. Our value exceeds this, so the data point can safely be neglected.

PROBLEMS

1. Assume the following discrete probability distribution:

x	0	1	2	3	4	5
p_x	0.00193	0.01832	0.1054	0.3679	0.7788	1.0000
	6	7	8	9	10	
	0.7788	0.3679	0.1054	0.01832	0.00193	

Find the mean and the standard deviation. Find the probability that x lies between $\langle x \rangle - \sigma_x$ and $\langle x \rangle - \sigma_x$.

$$\langle n \rangle = \frac{\sum_{n=0}^{10} np_n}{\sum_{n=0}^{10} p_n}$$

$$\begin{aligned} \sum_{n=0}^{10} p_n &= 2(0.00193) + 2(0.01832) + 2(0.1054) \\ &\quad + 2(0.3679) + 2(0.7788) + 1.000 \\ &= 3.5447 \end{aligned}$$

$$\sum_{n=0}^{10} np_n = (0+10)2(0.00193) + (1+9)2(0.01832)$$
$$+ (2+8)2(0.1054) + (3+7)2(0.3679)$$
$$+ (4+6)2(0.7788) + 1.000$$
$$= 17.723$$

$$\langle n \rangle = \frac{17.723}{3.5447} = 5.00$$
$$\langle n^2 \rangle = \frac{\sum_{n=0}^{10} n^2 p_n}{\sum_{n=0}^{10} p_n}$$
$$\sum_{n=0}^{10} n^2 p_n = 95.697$$
$$\langle n^2 \rangle = \frac{95.697}{3.5447} = 26.997$$
$$\sigma_n^2 = \langle n^2 \rangle - \langle n \rangle^2 = 26.997 - 25.00 = 1.0799$$
$$\sigma_n = \sqrt{1.0799} = 1.039$$

probability that x lies between $\langle x \rangle - \sigma_x$ and $\langle x \rangle - \sigma_x$

$$= \frac{1.000 + 2(0.7788)}{3.5447} = 0.722$$

2. Assume that a certain biased coin has a 51.0% probability of coming up "heads" when thrown.

a. Find the probability that in ten throws five "heads" will occur.

$$\text{probability} = \frac{10!}{5!5!}(0.510)^5(0.490)^5$$
$$= (252)(0.03450)(0.02825)$$
$$= 0.2456$$

b. Find the probability that in ten throws seven "heads" will occur.

$$\text{probability} = \frac{10!}{7!3!}(0.510)^7(0.490)^3$$
$$= (120)(0.008974)(0.11765)$$
$$= 0.1267$$

3. Calculate the mean and the standard deviation of all of the possible cases of ten throws for the biased coin in the previous problem. Let n be the number of "heads" in a given set of ten throws. Using Excel, we calculated the following:

n	*bin.* coeff.	$(0.510)^n (0.490)^{10-n}$	p_n	np_n	$n^2 p_n$
0	1	0.000797923	0.000797923	0	0
1	10	0.000830491	0.008304909	0.008304909	0.008304909
2	45	0.000864389	0.038897484	0.077794967	0.155589934
3	120	0.000899670	0.107960363	0.323881088	0.971643263
4	210	0.000936391	0.196642089	0.786568356	3.146273424
5	252	0.000974611	0.245601956	1.228009780	6.140048902
6	210	0.001014391	0.213022105	1.278132629	7.668795772
7	120	0.001055795	0.126695363	0.886867538	6.208072768
8	45	0.001098888	0.049449976	0.395599806	3.164798446
9	10	0.001143741	0.011437409	0.102936684	0.926430157
10	1	0.001190424	0.001190424	0.011904242	0.119042424

$$\langle n \rangle = \sum_{n=0}^{10} np_n = 5.100$$
$$\langle n^2 \rangle = \sum_{n=0}^{10} n^2 p_n = 28.509$$
$$\sigma_n^2 = \langle n^2 \rangle - \langle n \rangle^2 = 28.509 - 26.010 = 2.499$$
$$\sigma_n = \sqrt{2.499} = 1.580$$

The three values $n = 4$, $n = 5$, and $n = 6$ lie within one standard deviation of the mean, so that the probability that n lies within one standard deviation of the mean is equal to

$$\text{probability} = 0.196642 + 0.245602 + 0.213022$$
$$= 0.655266 = 65.53\%$$

This is close to the rule of thumb value of 2/3.

4. Consider the uniform probability distribution such that all values of x are equally probable in the range $-5.00 \prec x \prec 5.00$. Find the mean and the standard deviation. Compare these values with those found in the chapter for a uniform probability distribution in the range $0.00 \prec x \prec 10.00$.

$$\langle x \rangle = \frac{1}{2}(5.00 - 5.00) = 0.00$$
$$\sigma_x = \sigma_x^2 = \frac{1}{2\sqrt{3}}(5.00 + 5.00) = 2.8875$$

The mean is in the center of the range as expected, and the standard deviation is the same as in the case in the chapter.

5. Assume that a random variable, x, is governed by the probability distribution

$$f(x) = \frac{c}{x}$$

where x ranges from 1.00 to 10.00.

a. Find the mean value of x and its variance and standard deviation. We first find the value of c so that the distribution is normalized:

$$\begin{aligned}\int_{1.00}^{10.00}\frac{c}{x}\mathrm{d}x &= c\ln(x)|_{1.00}^{10.00}\\ &= c[\ln(10.00)-\ln(1.000)]\\ &= c\ln(10.00)\\ c &= \frac{1}{\ln(10.00)} = 0.43429\end{aligned}$$

$$\begin{aligned}\langle x\rangle &= \int_{1.00}^{10.00}x\frac{c}{x}\mathrm{d}x\\ &= c\int_{1.00}^{10.00}\mathrm{d}x = c(9.00)\\ &= \frac{9.00}{\ln(10.00)} = 3.909\\ \langle x^2\rangle &= \int_{1.00}^{10.00}x^2\frac{c}{x}\mathrm{d}x\\ &= c\int_{1.00}^{10.00}x\,\mathrm{d}x = \frac{c}{2}x^2\Big|_{1.00}^{10.00}\\ &= \frac{c}{2}(100.0-1.00)\\ &= \frac{99.0}{2\ln(10.00)} = 21.50\end{aligned}$$

$$\sigma_x^2 = \langle x^2\rangle - \langle x\rangle^2 = 21.50-(3.909)^2 = 6.220$$

$$\sigma_x = \sqrt{6.220} = 2.494$$

b. Find the probability that x lies between $\langle x\rangle-\sigma_x$ and $\langle x\rangle-\sigma_x$.

$$\begin{aligned}\text{probability} &= \int_{1.415}^{6.403}\frac{c}{x}\mathrm{d}x\\ &= c\ln(x)|_{1.415}^{6.403}\\ &= \frac{1}{\ln(10.00)}[\ln(6.403)-\ln(1.415)]\\ &= \frac{\ln(6.403/1.415)}{\ln(10.00)} = 0.6556\end{aligned}$$

This close to the rule of thumb value of 2/3.

6. Assume that a random variable, x, is governed by the probability distribution (a version of the Lorentzian function)

$$f(x) = \frac{c}{x^2+1}$$

where x ranges from -6.000 to 6.000.

a. Find the mean value of x and its variance and standard deviation. We first normalize the distribution:

$$\begin{aligned}1 &= c\int_{-6.000}^{6.000}\frac{1}{x^2+1}\mathrm{d}x\\ &= 2c\int_{0}^{6.000}\frac{1}{x^2+1}\mathrm{d}x\\ &= 2c\arctan(x)|_0^{6.000}\\ &= 2c[1.40565] = 2.8113c\\ c &= \frac{1}{2.8113} = 0.35571\end{aligned}$$

where we have used Eq. (11) of Appendix E.

$$\langle x\rangle = c\int_{-6.000}^{6.000}\frac{x}{x^2+1}\mathrm{d}x = 0$$

where have used the fact that the integrand is an odd function.

$$\begin{aligned}\langle x^2\rangle &= c\int_{-6.000}^{6.000}\frac{x^2}{x^2+1}\mathrm{d}x\\ &= 2c\int_{0}^{6.000}\frac{x^2}{x^2+1}\mathrm{d}x\\ &= 2c[x-\arctan(x)]|_0^{6.000}\\ &= 2c[6.000-\arctan(6.000)-0]\\ &= 2(0.35571)[6.000-1.40565] = 3.2685\end{aligned}$$

where we have used Eq. (13) of Appendix E.

$$\begin{aligned}\sigma_x^2 &= [\langle x^2\rangle - 0] = 3.2685\\ \sigma_x &= \sqrt{3.2685} = 1.8079\end{aligned}$$

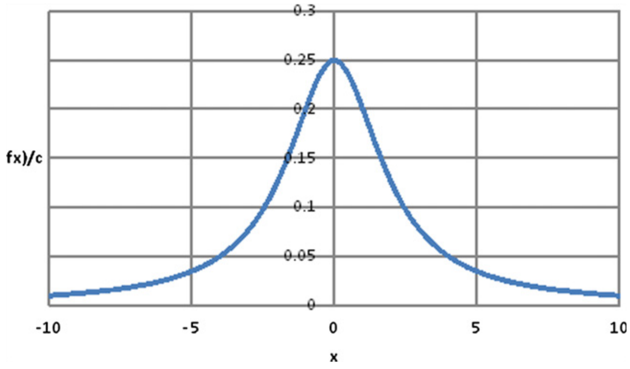
b. Find the probability that x lies between $\langle x\rangle-\sigma_x$ and $\langle x\rangle+\sigma_x$.

$$\begin{aligned}\text{probability} &= c\int_{-1.8079}^{1.8079}\frac{1}{x^2+1}\mathrm{d}x\\ &= 2c\int_{0}^{1.8079}\frac{1}{x^2+1}\mathrm{d}x\\ &= 2c\arctan(x)|_0^{1.8079}\\ &= 2c[1.06556]\\ &= 2(0.35571)(1.06556) = 0.7581\end{aligned}$$

7. Assume that a random variable, x, is governed by the probability distribution (a version of the Lorentzian function)

$$f(x) = \frac{c}{x^2+4}$$

where x ranges from -10.000 to 10.000. Here is a graph of the unnormalized function:



a. Find the mean value of x and its variance and standard deviation. We first normalize the distribution:

$$
\begin{aligned}
1 &= c\int_{-10.00}^{10.00}\frac{1}{x^2+4}\mathrm{d}x \\
&= 2c\int_{0}^{10.00}\frac{1}{x^2+4}\mathrm{d}x \\
&= 2c\left.\frac{\arctan(x/2)}{2}\right|_0^{10.00} = c[1.3734] \\
c &= \frac{1}{1.3734} = 0.72812
\end{aligned}
$$

where we have used Eq. (11) of Appendix E.

$$\langle x\rangle = c\int_{-10.00}^{10.00}\frac{x}{x^2+1}\mathrm{d}x = 0$$

where have used the fact that the integrand is an odd function.

$$
\begin{aligned}
\langle x^2\rangle &= c\int_{-10.00}^{10.00}\frac{x^2}{x^2+1}\mathrm{d}x = 2c\int_{0}^{10.00}\frac{x^2}{x^2+1}\mathrm{d}x \\
&= 2c\left[x-\frac{\arctan(x/2)}{2}\right]\Bigg|_0^{10.000} \\
&= 2c\left[10.000-\frac{\arctan(5.000)}{2}-0\right] \\
&= 2(0.72812)[10.000-0.68670] = 13.5624
\end{aligned}
$$

where we have used Eq. (13) of Appendix E.

$$
\begin{aligned}
\sigma_x^2 &= [\langle x^2\rangle - 0] = 13.562 \\
\sigma_x &= \sqrt{13.562} = 3.6827
\end{aligned}
$$

b. Find the probability that x lies between $\langle x\rangle - \sigma_x$ and $\langle x\rangle + \sigma_x$.

$$
\begin{aligned}
\text{probability} &= c\int_{-3.6827}^{3.6827}\frac{1}{x^2+4}\mathrm{d}x \\
&= 2c\int_{0}^{3.6827}\frac{1}{x^2+1}\mathrm{d}x \\
&= 2c\left.\frac{\arctan(x/2)}{2}\right|_0^{3.6827} \\
&= c[1.07328] \\
&= (0.72812)(1.07328) = 0.7815
\end{aligned}
$$

8. Find the probability that x lies between $\mu - 1.500\sigma$ and $\mu + 1.500\sigma$ for a Gaussian distribution.

$$
\begin{aligned}
\text{fraction} &= \frac{1}{\sqrt{2\pi}\sigma}\int_{\mu-1.500\sigma}^{\mu+1.500\sigma} e^{-(x-\mu)^2/2\sigma^2}\,\mathrm{d}x \\
&= \frac{1}{\sqrt{2\pi}\sigma}\int_{-1.500\sigma}^{1.500\sigma} e^{-y^2/2\sigma^2}\,\mathrm{d}y \\
&= \frac{1}{\sqrt{2\pi}\sigma}\int_{0}^{1.500\sigma} e^{-y^2/2\sigma^2}\,\mathrm{d}y
\end{aligned}
$$

Let $u = \dfrac{y}{\sqrt{2}\sigma}$

$$y = 1.500\sigma \leftrightarrow u = \frac{1.500\sigma}{\sqrt{2}\sigma} = 1.061$$

$$
\begin{aligned}
\text{fraction} &= \frac{\sqrt{2}\sigma}{\sqrt{2\pi}\sigma}\int_0^{1.061} e^{-u^2}\,\mathrm{d}u \\
&= \frac{1}{\sqrt{\pi}}\int_0^{1.061} e^{-u^2}\,\mathrm{d}u \\
&= \mathrm{erf}(1.061) = 0.8662
\end{aligned}
$$

9. The nth moment of a probability distribution is defined by

$$M_n = \int (x-\mu)^n f(x)\mathrm{d}x.$$

The second moment is the variance, or square of the standard deviation. Show that for the Gaussian distribution, $M_3 = 0$, and find the value of M_4, the fourth moment. Find the value of the fourth root of M_4.

$$
\begin{aligned}
M_3 &= \int_{-\infty}^{\infty}(x-\mu)^3\frac{1}{\sqrt{2\pi}\sigma}e^{-(x-\mu)^2/2\sigma^2}\,\mathrm{d}x \\
&= \int_{-\infty}^{\infty} y^3\frac{1}{\sqrt{2\pi}\sigma}e^{-y^2/2\sigma^2}\,\mathrm{d}x = 0
\end{aligned}
$$

where we have let $y = x-\mu$, and where we set the integral equal to zero since its integrand is an odd function.

$$\begin{aligned}M_4 &= \int_{-\infty}^{\infty} (x-\mu)^4 \frac{1}{\sqrt{2\pi}\sigma} e^{-(x-\mu)^2/2\sigma^2}\,\mathrm{d}x \\ &= \int_{-\infty}^{\infty} y^4 \frac{1}{\sqrt{2\pi}\sigma} e^{-y^2/2\sigma^2}\,\mathrm{d}x \\ &= \frac{2}{\sqrt{2\pi}\sigma}\int_0^{\infty} y^4 e^{-y^2/2\sigma^2}\,\mathrm{d}x\end{aligned}$$

where have recognized that the integrand is an even function. From Eq. (23) of Appendix F,

$$\int_0^{\infty} x^{2n} e^{-r^2x^2}\,\mathrm{d}x = \frac{(1)(3)(5)\cdots(2n-1)}{2^{n+1}r^{2n+1}}\sqrt{\pi}$$

so that

$$\begin{aligned}\int_0^{\infty} x^4 e^{-r^2x^2}\,\mathrm{d}x &= \frac{(1)(3)}{2^3r^5}\sqrt{\pi} \\ M_4 &= \frac{2}{\sqrt{2\pi}\sigma}\frac{3}{8}(2\sigma^2)^{5/2}\sqrt{\pi} = 3\sigma^4 \\ M_4^{1/4} &= \sqrt[4]{3}\sigma = 1.316\sigma\end{aligned}$$

10. Find the third and fourth moments (defined in the previous problem) for the uniform probability distribution such that all values of x in the range $-5.00 \prec x \prec 5.00$ are equally probable. Find the value of the fourth root of M_4. Find the value of the fourth root of M_4.

$$\begin{aligned}M_3 &= \frac{1}{10.00}\int_{-5.00}^{5.00} x^3\,\mathrm{d}x \\ &= \frac{1}{10.00}\frac{x^4}{4}\bigg|_{-5.00}^{5.00} \\ &= \frac{1}{10.00}\left[\frac{(5.00)^4}{4} - \frac{(5.00)^4}{4}\right] = 0.00 \\ M_4 &= \frac{1}{10.00}\int_{-5.00}^{5.00} x^4\,\mathrm{d}x \\ &= \frac{1}{10.00}\frac{x^5}{5}\bigg|_{-5.00}^{5.00} \\ &= \frac{1}{10.00}\left[\frac{(5.00)^5}{5} - \frac{(-5.00)^5}{5}\right] = 125.0\end{aligned}$$

$$M_4^{1/4} = \sqrt[4]{125.0} = 3.344$$

11. A sample of 10 sheets of paper has been selected randomly from a ream (500 sheets) of paper. The width and length of each sheet of the sample were measured, with the following results:

Sheet number	Width/in	Length/in
1	8.50	11.03
2	8.48	10.99
3	8.51	10.98
4	8.49	11.00
5	8.50	11.01
6	8.48	11.02
7	8.52	10.98
8	8.47	11.04
9	8.53	10.97
10	8.51	11.00

a. Calculate the sample mean width and its sample standard deviation, and the sample mean length and its sample standard deviation.

$$\begin{aligned}\langle w\rangle &= \frac{1}{10}(8.50\text{ in} + 8.48\text{ in} + 8.51\text{ in} + 8.49\text{ in} \\ &\quad + 8.50\text{ in} + 8.48\text{ in} + 8.52\text{ in} + 8.47\text{ in} \\ &\quad + 8.53\text{ in} + 8.51\text{ in}) = 8.499\text{ in} \\ s_w &= \left\{\frac{1}{9}\left[(0.00\text{ in})^2 + (0.02\text{ in})^2 + (0.01\text{ in})^2\right.\right. \\ &\quad + (0.01\text{ in})^2 + (0.00\text{ in})^2 + (0.02\text{ in})^2 \\ &\quad + (0.02\text{ in})^2 + (0.03\text{ in})^2 \\ &\quad \left.\left. + (0.03\text{ in})^2 + (0.01\text{ in})^2\right]\right\}^{1/2} \\ &= 0.019\text{ in}\end{aligned}$$

$$\begin{aligned}\langle l\rangle &= \frac{1}{10}(11.03\text{ in} + 10.99\text{ in} + 10.98\text{ in} \\ &\quad + 11.00\text{ in} + 11.01\text{ in} + 11.02\text{ in} \\ &\quad + 10.98\text{ in} + 11.04\text{ in} \\ &\quad + 10.97\text{ in} + 11.00\text{ in}) = 11.002\text{ in}\end{aligned}$$

$$\begin{aligned}s_l &= \left\{\frac{1}{9}\left[(0.03\text{ in})^2 + (0.01\text{ in})^2 + (0.02\text{ in})^2\right.\right. \\ &\quad + (0.00\text{ in})^2 + (0.01\text{ in})^2 + (0.02\text{ in})^2 \\ &\quad + (0.02\text{ in})^2 + (0.04\text{ in})^2 + (0.03\text{ in})^2 \\ &\quad \left.\left. + (0.00\text{ in})^2\right]\right\}^{1/2} = 0.023\text{ in}\end{aligned}$$

b. Give the expected error in the width and length at the 95% confidence level.

$$\begin{aligned}\varepsilon_w &= \frac{(2.262)(0.019\text{ in})}{\sqrt{10}} = 0.014\text{ in} \\ \varepsilon_l &= \frac{(2.262)(0.023\text{ in})}{\sqrt{10}} = 0.016\text{ in}\end{aligned}$$

$$\begin{aligned}w &= 8.50\text{ in} \pm 0.02\text{ in} \\ l &= 11.01\text{ in} \pm 0.02\text{ in}\end{aligned}$$

c. Calculate the expected real mean area from the width and length.

$$A = (8.499\ \text{in})(11.002\ \text{in}) = 93.506\ \text{in}^2$$

d. Calculate the area of each sheet in the sample. Calculate from these areas the sample mean area and the standard deviation in the area.

Sheet number	Width/in	Length/in	Area/in^2
1	8.50	11.03	93.755
2	8.48	10.99	93.1952
3	8.51	10.98	93.4398
4	8.49	11.00	93.39
5	8.50	11.01	93.585
6	8.48	11.02	93.4496
7	8.52	10.98	93.5496
8	8.47	11.04	93.5088
9	8.53	10.97	93.5741
10	8.51	11.00	93.61

$$\langle A\rangle = 93.506\ \text{in}^2$$
$$s_A = 0.150\ \text{in}^2$$

e. Give the expected error in the area from the results of part *d*.

$$\varepsilon_A = \frac{(2.262)(0.159\ \text{in})}{\sqrt{10}} = 0.114\ \text{in}^2$$

12. A certain harmonic oscillator has a position given as a function of time by

$$z = (0.150\ \text{m})[\sin(\omega t)]$$

where

$$\omega = \sqrt{\frac{k}{m}}.$$

The value of the force constant k is 0.455 N m^{-1} and the mass of the oscillator m is 0.544 kg. Find time average of the potential energy of the oscillator over 1.00 period of the oscillator. How does the time average compare with the maximum value of the potential energy?

$$\omega = \left(\frac{0.455\ \text{N m}^{-1}}{0.544\ \text{kg}}\right) = 0.915\ \text{s}^{-1}$$
$$\tau = \frac{1}{\nu} = \frac{2\pi}{\omega} = 6.87\ \text{s}$$
$$\mathcal{V} = \frac{1}{2}kz^2$$

$$\overline{\mathcal{V}} = \left(\frac{1}{6.87\ \text{s}}\right)\frac{1}{2}(0.455\ \text{N m}^{-1})(0.150\ \text{m})^2 \times \int_0^{6.87\ \text{s}} \sin^2\left[(0.915\ \text{s}^{-1})t\right]\text{d}t$$

Let $u = (0.915\ \text{s}^{-1})t$.

$$\begin{aligned}\overline{\mathcal{V}} &= \left(\frac{1}{6.87\ \text{s}}\right)\frac{1}{2}(0.455\ \text{N m}^{-1})(0.150\ \text{m})^2 \times \left(\frac{1}{0.915\ \text{s}^{-1}}\right)\int_0^{2\pi}\sin^2(u)\text{d}t \\ &= (0.0008143\ \text{N m})\left[\frac{u}{2} - \frac{\sin(2u)}{4}\right]\Bigg|_0^{2\pi} \\ &= (0.0008143\ \text{N m})\pi = 0.00256\ \text{J}\end{aligned}$$

The time average is equal to $\frac{1}{2}$ of the maximum value of the potential energy:

$$\begin{aligned}\mathcal{V}_{\text{max}} &= \frac{1}{2}kz_{\text{max}}^2 = \frac{1}{2}(0.455\ \text{N m}^{-1})(0.150\ \text{m})^2 \\ &= 0.00512\ \text{J}\end{aligned}$$

13. A certain harmonic oscillator has a position given by

$$z = (0.150\ \text{m})[\sin(\omega t)]$$

where

$$\omega = \sqrt{\frac{k}{m}}.$$

The value of the force constant k is 0.455 N m^{-1} and the mass of the oscillator m is 0.544 kg. Find time average of the kinetic energy of the oscillator over 1.00 period of the oscillator. How does the time average compare with the maximum value of the kinetic energy?A certain harmonic oscillator has a position given by

$$z = (0.150\ \text{m})[\sin(\omega t)]$$

where

$$\omega = \sqrt{\frac{k}{m}}.$$

The value of the force constant k is 0.455 N m^{-1} and the mass of the oscillator m is 0.544 kg. Find time average of the kinetic energy of the oscillator over 1.00 period of the oscillator. How does the time average compare with the maximum value of the kinetic energy?

$$\omega = \left(\frac{0.455\ \text{N m}^{-1}}{0.544\ \text{kg}}\right) = 0.915\ \text{s}^{-1}$$

$$\begin{aligned}v &= \frac{\text{d}z}{\text{d}t} = (0.150\ \text{m})\omega[\cos(\omega t)] \\ &= (0.150\ \text{m})(0.915\ \text{s}^{-1})[\cos(\omega t)] \\ &= (0.1372\ \text{m s}^{-1})\cos[(0.915\ \text{s}^{-1})t]\end{aligned}$$

$$\tau = \frac{1}{\nu} = \frac{2\pi}{\omega} = 6.87 \text{ s}$$
$$\mathcal{K} = \frac{1}{2}mv^2$$

$$\overline{K} = \left(\frac{1}{6.87 \text{ s}}\right)\frac{1}{2}(0.544 \text{ kg})(0.1372 \text{ m s}^{-1})^2 \times \int_0^{6.87 \text{ s}} \cos^2\left[(0.915 \text{ s}^{-1})t\right] \mathrm{d}t$$

Let $u = (0.915 \text{ s}^{-1})t$.

$$\begin{aligned}\overline{\mathcal{K}} &= \left(\frac{1}{6.87 \text{ s}}\right)\frac{1}{2}(0.544 \text{ kg})(0.1372 \text{ m s}^{-1})^2 \\ &\quad\times \left(\frac{1}{0.915 \text{ s}^{-1}}\right)\int_0^{2\pi} \cos^2(u)\mathrm{d}t \\ &= (0.0008143 \text{ kg m}^2\text{s}^{-2})\left[\frac{u}{2} + \frac{\sin(2u)}{4}\right]\Bigg|_0^{2\pi} \\ &= (0.0008143 \text{ kg m}^2 \text{ s}^{-2})\pi = 0.00256 \text{ J}\end{aligned}$$

The time average is equal to $\frac{1}{2}$ of the maximum value of the kinetic energy:

$$\begin{aligned}\mathcal{V}_{\text{max}} &= \frac{1}{2}kz_{\text{max}}^2 = \frac{1}{2}(0.544 \text{ kg})(0.1372 \text{ m s}^{-1})^2 \\ &= 0.00512 \text{ J}\end{aligned}$$

14. The following measurements of a given variable have been obtained: 23.2, 24.5, 23.8, 23.2, 23.9, 23.5, 24.0. Apply the Q test to see if one of the data points can be disregarded. Calculate the mean of these values, excluding the suspect value if one can be disregarded.

$$Q = \frac{0.5}{1.3} = 0.38$$

The critical value of Q for a set of 6 members is equal to 0.63. No data point can be disregarded. The mean is

$$\begin{aligned}\text{mean} &= \frac{1}{7}(23.2 + 24.5 + 23.8 \\ &\quad + 23.2 + 23.9 + 23.5 + 24.0) \\ &= 23.73\end{aligned}$$

15. The following measurements of a given variable have been obtained: 68.25, 68.36, 68.12, 68.40, 69.20, 68.53, 68.18, 68.32. Apply the Q test to see if one of the data points can be disregarded.

The suspect data point is equal to 69.20. The closest value to it is equal to 68.53 and the range from the highest to the lowest is equal to 1.08.

$$Q = \frac{0.67}{1.08} = 0.62$$

The critical value of Q for a set of 8 members is equal to 0.53. The fifth value, 69.20, can safely be disregarded. The mean of the remaining values is

$$\begin{aligned}\text{mean} &= \frac{1}{7}(68.25 + 68.36 + 68.12, 68.40 \\ &\quad + 68.53 + 68.18 + 68.32) \\ &= 68.31\end{aligned}$$

Data Reduction and the Propagation of Errors

EXERCISES

Exercise 16.1. Two time intervals have been clocked as $t_1 = 6.57\ \text{s} \pm 0.13\ \text{s}$ and $t_2 = 75.12\ \text{s} \pm 0.17\ \text{s}$. Find the probable value of their sum and its probable error. Let $t = t_1 + t_2$.

$$\bar{t} = 56.57\ \text{s} + 75.12\ \text{s} = 131.69\ \text{s}$$
$$\varepsilon_t = [(0.13\ \text{s})^2 + (0.17\ \text{s})^2]^{1/2} = 0.21\ \text{s}$$
$$t = 131.69\ \text{s} \pm 0.21\ \text{s}$$

Exercise 16.2. Assume that you estimate the total systematic error in a melting temperature measurement as 0.20 °C at the 95% confidence level and that the random error has been determined to be 0.06 °C at the same confidence level. Find the total expected error.

$$\varepsilon_t = [(0.06\ ^\circ\text{C})^2 + (0.20\ ^\circ\text{C})^2]^{1/2} = 0.21\ ^\circ\text{C}.$$

Notice that the random error, which is 30% as large as the systematic error, makes only a 5% contribution to the total error.

Exercise 16.3. In the cryoscopic determination of molar mass,[1] the molar mass in kg mol^{-1} is given by

$$M = \frac{wK_f}{W\Delta T_\text{f}}(1 - k_f\Delta T_\text{f}),$$

where W is the mass of the solvent in kilograms, w is the mass of the unknown solute in kilograms, ΔT_f is the amount by which the freezing point of the solution is less than that of the pure solvent, and K_f and k_f are constants characteristic of the solvent. Assume that in a given experiment, a sample of an unknown substance was dissolved in benzene, for which $K_f = 5.12$ K kg mol^{-1} and $k_f = 0.011$ K^{-1}. For the following data, calculate M and its probable error:

$$\begin{aligned}
W &= 13.185 \pm 0.003\ \text{g}\\
w &= 0.423 \pm 0.002\ \text{g}\\
\Delta T_\text{f} &= 1.263 \pm 0.020\ \text{K}.\\
M &= \frac{wK_f}{W\Delta T_\text{f}}(1 - k_f\Delta T_\text{f})\\
&= \frac{(0.423\ \text{g})(5.12\ \text{K kg mol}^{-1})}{(13.185\ \text{g})(1.263\ \text{K})}\\
&\quad \times[1 - (0.011\ \text{K}^{-1})(1.263\ \text{K})]\\
&= (0.13005\ \text{kg mol}^{-1})[1 - 0.01389]\\
&= 0.12825\ \text{kg mol}^{-1} = 128.25\ \text{g mol}^{-1}
\end{aligned}$$

We assume that errors in K_f and k_f are negligible.

$$\begin{aligned}
\frac{\partial M}{\partial w} &= \frac{K_f}{W\Delta T_\text{f}}(1 - k_f\Delta T_\text{f})\\
&= \frac{(5.12\ \text{K kg mol}^{-1})}{(13.185\ \text{g})(1.263\ \text{K})}\\
&\quad \times[1 - (0.011\ \text{K}^{-1})(1.263\ \text{K})]\\
&= 0.30319\ \text{kg mol}^{-1}\ \text{g}^{-1}\\
\frac{\partial M}{\partial W} &= -\frac{wK_f}{W^2\Delta T_\text{f}}(1 - k_f\Delta T_\text{f})\\
&= \frac{(0.423\ \text{g})(5.12\ \text{K kg mol}^{-1})}{(13.185\ \text{g})^2(1.263\ \text{K})}
\end{aligned}$$

[1] Carl W. Garland, Joseph W. Nibler, and David P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., p. 182, McGraw-Hill, New York, 2003.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00040-9

$$
\begin{aligned}
&\times[1-(0.011\ \mathrm{K}^{-1})(1.263\ \mathrm{K})]\\
&= 0.00973\ \mathrm{kg\ mol^{-1}\ g^{-1}}\\
\frac{\partial M}{\partial \Delta T_{\mathrm{f}}} &= -\frac{wK_f}{W(\mathbf{1}T_{\mathrm{f}})^2}(1-k_f\mathbf{\Delta}T_{\mathrm{f}})-\frac{wK_f}{W\mathbf{\Delta}T_{\mathrm{f}}}(k_f)\\
&= \frac{(0.423\ \mathrm{g})(5.12\ \mathrm{K\ kg\ mol^{-1}})}{(13.185\ \mathrm{g})(1.263\ \mathrm{K})^2}\\
&\times[1-(0.011\ \mathrm{K}^{-1})(1.263\ \mathrm{K})]\\
&-\frac{(0.423\ \mathrm{g})(5.12\ \mathrm{K\ kg\ mol^{-1}})(0.011\ \mathrm{K^{-1}})}{(13.185\ \mathrm{g})(1.263\ \mathrm{K})}\\
&= 0.10154\ \mathrm{kg\ mol^{-1}\ K^{-1}} - 0.00143\ \mathrm{kg\ mol^{-1}\ K^{-1}}\\
&= 0.10011\ \mathrm{kg\ mol^{-1}\ K^{-1}}\\
\varepsilon_M &= [(0.30319\ \mathrm{kg\ mol^{-1}\ g^{-1}})^2 0.002\ \mathrm{g})^2\\
&+(0.00973\ \mathrm{kg\ mol^{-1}\ g^{-1}})^2(0.003\ \mathrm{g})^2\\
&+(0.10011\ \mathrm{kg\ mol^{-1}\ K^{-1}})^2(0.020\ \mathrm{K})^2]^{1/2}\\
&= [3.68\times10^{-7}\ \mathrm{kg^2\ mol^{-2}}\\
&+8.52\times10^{-10}\ \mathrm{kg^2\ mol^{-2}}\\
&+4.008\times10^{-6}\ \mathrm{kg^2\ mol^{-2}}]^{1/2}\\
&= 0.00209\ \mathrm{kg\ mol^{-1}}\\
M &= 0.128\ \mathrm{kg\ mol^{-1}} \pm 0.002\ \mathrm{kg\ mol^{-1}}\\
&= 128\ \mathrm{g\ mol^{-1}} \pm 2\ \mathrm{g\ mol^{-1}}
\end{aligned}
$$

The principal source of error was in the measurement of ΔT_{f}.

Exercise 16.4. The following data give the vapor pressure of water at various temperatures.[2] Transform the data, using $\ln(P)$ for the dependent variable and $1/T$ for the independent variable. Carry out the least squares fit by hand, calculating the four sums. Find the molar enthalpy change of vaporization.

Temperature/°C	Vapor pressure/torr
0	4.579
5	6.543
10	9.209
15	12.788
20	17.535
25	23.756

[2] R. Weast, Ed., *Handbook of Chemistry and Physics*, 51st ed., p. D-143, CRC Press, Boca Raton, FL, 1971–1972.

$1/(T/\mathrm{K})$	$\ln(P/\mathrm{torr})$
0.003354	3.167835
0.003411	2.864199
0.003470	2.548507
0.003532	2.220181
0.003595	1.878396
0.003661	1.521481

$$
\begin{aligned}
S_x &= 0.02102\\
S_y &= 14.200\\
S_{xy} &= 0.04940\\
S_{x^2} &= 7.373\times10^{-5}
\end{aligned}
$$

$$
\begin{aligned}
D &= NS_{x^2}-S_x^2 = 6(7.373\times10^{-5})-(0.02102)^2\\
&= 3.9575\times10^{-7}\\
m &= \frac{NS_{xy}-S_xS_y}{D}\\
&= \frac{[6(0.049404)-(0.021024)(14.2006)]}{3.95751\times10^{-7}} = -5362\ \mathrm{K}\\
b &= \frac{S_{x^2}S_y-S_xS_{xy}}{D}\\
&= \frac{(7.46607\times10^{-5})(14.2006)-(0.021024)(0.049404)}{3.95751\times10^{-7}}\\
&= 21.156
\end{aligned}
$$

Our value for the molar enthalpy change of vaporization is

$$
\begin{aligned}
\mathbf{\Delta}H_{\mathrm{m}} &= -mR = -(-5362\ \mathrm{K})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\\
&= 44.6\times10^3\ \mathrm{J\ mol^{-1}} = 44.6\ \mathrm{kJ\ mol^{-1}}
\end{aligned}
$$

Exercise 16.5. Calculate the covariance for the following ordered pairs:

y	x
−1.00	0.00
0	1.00
1.00	0.00
0.00	−1.00

$$
\begin{aligned}
\langle x\rangle &= 0.00\\
\langle y\rangle &= 0.00
\end{aligned}
$$

$$
s_{x,y} = \frac{1}{3}(0.00+0.00+0.00+0.00) = 0
$$

Exercise 16.6. Assume that the expected error in the logarithm of each concentration in Example 16.5 is equal to 0.010. Find the expected error in the rate constant, assuming the reaction to be first order.

$$D = NS_{x^2} - S_x^2 = 9(7125) - (225)^2 = 13500\ \text{min}^2$$

$$\varepsilon_m = \left(\frac{9}{13500\ \text{min}}\right)^{1/2}(0.010) = 2.6 \times 10^{-4}\ \text{min}^{-1}$$

$$m = -0.03504\ \text{min}^{-1} \pm 0.0003\ \text{min}^{-1}$$
$$k = 0.0350\ \text{min}^{-1} \pm 0.0003\ \text{min}^{-1}$$

Exercise 16.7. Sum the residuals in Example 16.5 and show that this sum vanishes in each of the three least-square fits. For the first-order fit

$$\begin{array}{ll} r_1 = -0.00109 & r_6 = 0.00634 \\ r_2 = 0.00207 & r_7 = -0.00480 \\ r_3 = -0.00639 & r_8 = 0.01891 \\ r_4 = -0.00994 & r_9 = -0.01859. \\ r_5 = 0.01348 & \end{array}$$
$$sum = -0.00001 \approx 0$$

For the second-order fit

$$\begin{array}{ll} r_1 = 0.3882 & r_6 = -0.3062 \\ r_2 = 0.1249 & r_7 = -0.1492 \\ r_3 = -0.0660 & r_8 = -0.0182 \\ r_4 = -0.2012 & r_9 = 0.5634. \\ r_5 = -0.3359 & \end{array}$$
$$sum = -0.00020 \approx 0$$

For the third-order fit

$$\begin{array}{ll} r_1 = 2.2589 & r_6 = -2.0285 \\ r_2 = 0.8876 & r_5 = -1.2927 \\ r_3 = -0.2631 & r_8 = -0.2121 \\ r_4 = -1.1901 & r_9 = 3.8031. \\ r_5 = -1.9531 & \end{array}$$
$$sum = 0.0101 \approx 0$$

There is apparently some round-off error.

Exercise 16.8. Assuming that the reaction in Example 16.5 is first order, find the expected error in the rate constant, using the residuals as estimates of the errors. Here are the residuals, obtained by a least-squares fit in an Excel worksheet.

$$\begin{array}{ll} r_1 = -0.00109 & r_6 = 0.00634 \\ r_2 = 0.00207 & r_7 = -0.00480 \\ r_3 = -0.00639 & r_8 = 0.01891 \\ r_4 = -0.00994 & r_9 = -0.01859. \\ r_5 = 0.01348 & \end{array}$$

The standard deviation of the residuals is

$$s_r^2 = \frac{1}{7}\sum_{i=1}^{9} r_1^2 = \frac{1}{7}(0.001093)$$
$$s_r = 0.033064$$

$$D = NS_{x^2} - S_x^2 = 9(7125) - (225)^2 = 13500\ \text{min}^2$$

$$\begin{aligned} \varepsilon_m &= \left(\frac{N}{D}\right)^{1/2} t(\nu, 0.05)s_r \\ &= \left(\frac{9}{13500\ \text{min}^2}\right)^{1/2}(2.365)(0.033064) \\ &= 0.0020\ \text{min}^{-1} \end{aligned}$$

$$k = 0.0350\ \text{min}^{-1} \pm 0.002\ \text{min}^{-1}$$

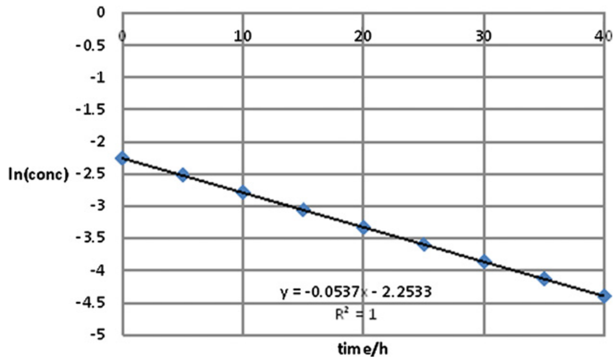
Exercise 16.9. The following is a set of data for the following reaction at 25 °C.[3]

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$$

Time/h	$[(CH_3)_3CBr]$/mol l^{-1}
0	0.1051
5	0.0803
10	0.0614
15	0.0470
20	0.0359
25	0.0274
30	0.0210
35	0.0160
40	0.0123

3 L. C. Bateman, E. D. Hughes, and C. K. Ingold, "*Mechanism of Substitution at a Saturated Carbon Atom. Pm XIX. A Kinetic Demonstration of the Unimolecular Solvolysis of Alkyl Halides*," J. Chem. Soc. 960 (1940).

Using linear least squares, determine whether the reaction obeys first-order, second-order, or third-order kinetics and find the value of the rate constant.
To test for first order, we create a spreadsheet with the time in one column and the natural logarithm of the concentration in the next column. A linear fit on the graph gives the following:



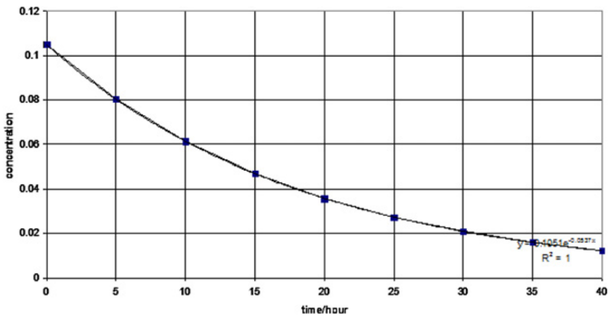
$$\ln(conc) = -(0.0537)t - 2.2533$$

with a correlation coefficient equal to 1.00. The fit gives a value of the rate constant

$$k = 0.0537 \text{ h}^{-1}$$

To test for second order, we create a spreadsheet with the time in one column and the reciprocal of the concentration in the next column. This yielded a set of points with an obvious curvature and a correlation coefficient squared for the linear fit equal to 0.9198. The first order fit is better. To test for third order, we created a spreadsheet with the time in one column and the reciprocal of the square of the concentration in the next column. This yielded a set of points with an obvious curvature and a correlation coefficient squared for the linear fit equal to 0.7647. The first order fit is the best fit.

Exercise 16.10. Take the data from the previous exercise and test for first order by carrying out an exponential fit using Excel. Find the value of the rate constant. Here is the graph



The function fit to the data is

$$c = (0.1051 \text{ mol l}^{-1})e^{-0.0537t}$$

so that the rate constant is

$$k = 0.0537 \text{ h}^{-1}$$

which agrees with the result of the previous exercise.

Exercise 16.11. Change the data set of Table 16.1 by adding a value of the vapor pressure at 70 °C of 421 torr ± 40 torr. Find the least-squares line using both the unweighted and weighted procedures. After the point was added, the results were as follows: For the unweighted procedure,

$$m = \text{slope} = -4752 \text{ K}$$
$$b = \text{intercept} = 19.95;$$

For the weighted procedure,

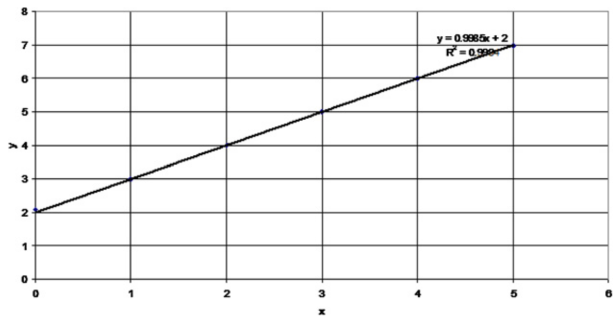
$$m = \text{slope} = -4855 \text{ K}$$
$$b = \text{intercept} = 20.28.$$

Compare these values with those obtained in the earlier example: $m = \text{slope} = -4854$ K, and $b = \text{intercept} = 20.28$. The spurious data point has done less damage in the weighted procedure than in the unweighted procedure.

Exercise 16.12. Carry out a linear least squares fit on the following data, once with the intercept fixed at zero and one without specifying the intercept:

x	0	1	2	3	4	5
y	2.10	2.99	4.01	4.99	6.01	6.98

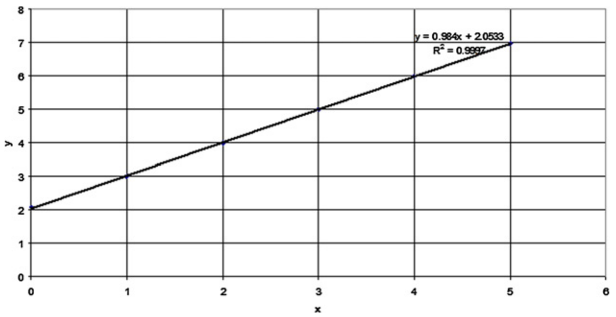
Compare your slopes and your correlation coefficients for the two fits. With the intercept set equal to 2.00, the fit is



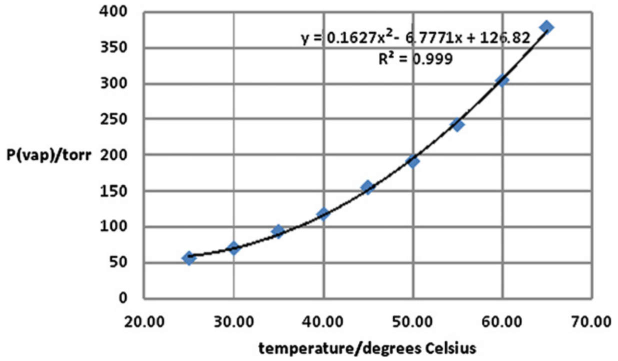
$$y = 0.9985x + 2.00$$
$$r^2 = 0.9994$$

Without specifying the intercept, the fit is

$$y = 0.984x + 2.0533$$
$$r^2 = 0.9997$$



Exercise 16.13. Fit the data of the previous example to a quadratic function (polynomial of degree 2) and repeat the calculation. Here is the fit to a graph, obtained with Excel



$$P = 0.1627t^2 - 6.7771t + 126.82$$

where we omit the units.

$$\frac{dP}{dt} = 0.3254t - 6.7771$$

This gives a value of 7.8659 torr $°C^{-1}$ for dP/dt at 45 °C.

$$\begin{aligned}\Delta H_m &= (T\Delta V_m)\left(\frac{dP}{dT}\right) = (318.15\ \text{K})(0.1287\ \text{m}^3\ \text{mol}^{-1})\\ &\quad\times(7.8659\ \text{torr K}^{-1})\left(\frac{101325\ \text{J m}^{-3}}{760\ \text{torr}}\right)\\ &= 4.294\times10^4\ \text{J mol}^{-1} = 42.94\ \text{kJ mol}^{-1}\end{aligned}$$

This is less accurate than the fit to a fourth-degree polynomial in the example.

PROBLEMS

1. In order to determine the intrinsic viscosity $[\eta]$ of a solution of polyvinyl alcohol, the viscosities of several solutions with different concentrations are measured. The intrinsic viscosity is defined as the limit[4]

$$\lim_{c\to 0}\left(\frac{1}{c}\ln\left(\frac{\eta}{\eta_0}\right)\right)$$

where c is the concentration of the polymer measured in grams per deciliter, η is the viscosity of a solution of concentration c, and η_0 is the viscosity of the pure solvent (water in this case). The intrinsic viscosity and the viscosity-average molar mass are related by the formula

$$[\eta] = (2.00\times10^{-4}\ \text{dl g}^{-1})\left(\frac{M}{M_0}\right)^{0.76}$$

where M is the molar mass and $M_0 = 1$ g mol^{-1} (1 dalton). Find the molar mass if $[\eta] = 0.86$ dl g^{-1}. Find the expected error in the molar mass if the expected error in $[\eta]$ is 0.03 dl g^{-1}.

$$\frac{[\eta]}{(2.00\times10^{-4}\ \text{dl g}^{-1})} = \left(\frac{M}{M_0}\right)^{0.76}$$

$$\begin{aligned}\left(\frac{M}{M_0}\right) &= \left(\frac{[\eta]}{(2.00\times10^{-4}\ \text{dl g}^{-1})}\right)^{1/0.76}\\ &= \left(\frac{[\eta]}{(2.00\times10^{-4}\ \text{dl g}^{-1})}\right)^{1.32}\\ M &= (1\ \text{g mol}^{-1})\left(\frac{0.86\ \text{dl g}^{-1}}{(2.00\times10^{-4}\ \text{dl g}^{-1})}\right)^{1.32}\\ &= 6.25\times10^4\ \text{g mol}^{-1}\end{aligned}$$

$$\begin{aligned}\varepsilon_M &= \left|\frac{\partial M}{\partial[\eta]}\right|\varepsilon_{[\eta]}\\ &= 1.32M_0(5.00\times10^3\ \text{g dl}^{-1})^{1.32}[\eta]^{0.32}\varepsilon_{[\eta]}\\ &= (1.32)(1\ \text{g mol}^{-1})(5.00\times10^3\ \text{g dl}^{-1})^{1.32}\\ &\quad\times(0.86\ \text{dl g}^{-1})^{0.32}(0.03\ \text{dl g}^{-1})\\ &= 2.2\times10^3\ \text{g mol}^{-1}\end{aligned}$$

Assume that the error in the constants M_0 and 2.00×10^{-4} dl g^{-1} is negligible.

2. Assuming that the ideal gas law holds, find the amount of nitrogen gas in a container if

$$\begin{aligned}P &= 0.836\ \text{atm} \pm 0.003\ \text{atm}\\ V &= 0.01985\ \text{m}^3 \pm 0.00008\ \text{m}^3\\ T &= 29.3\ \text{K} \pm 0.2\ \text{K}.\end{aligned}$$

[4] Carl W. Garland, Joseph W. Nibler, and David P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., McGraw-Hill, New York, 2003, pp. 321–323.

Find the expected error in the amount of nitrogen.

$$\begin{aligned}
n &= \frac{PV}{RT} \\
&= \frac{(0.836\ \text{atm})(101325\ \text{J m}^{-3}\ \text{atm}^{-1})(0.01985\ \text{m}^3)}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.3\ \text{K})} \\
&= 0.6779\ \text{mol} \\
\varepsilon_n &\approx \left[\left(\frac{\partial n}{\partial P}\right)^2 \varepsilon_P^2 + \left(\frac{\partial n}{\partial T}\right)^2 \varepsilon_T^2 + \left(\frac{\partial n}{\partial V}\right)^2 \varepsilon_V^2\right]^{1/2} \\
\left(\frac{\partial n}{\partial P}\right)_{T,V} &= \frac{V}{RT} = \frac{(0.01985\ \text{m}^3)}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.3\ \text{K})} \\
&= 5.53 \times 10^{-4}\ \text{mol J}^{-1}\ \text{m}^3 = 8.003 \times 10^{-6}\ \text{mol Pa}^{-1} \\
\left(\frac{\partial n}{\partial T}\right)_{P,V} &= -\frac{PV}{RT^2} \\
&= -\frac{(0.836\ \text{atm})(101325\ \text{J m}^{-3}\ \text{atm}^{-1})(0.01985\ \text{m}^3)}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.3\ \text{K})^2} \\
&= -2.273 \times 10^{-3}\ \text{mol K}^{-1} \\
\left(\frac{\partial n}{\partial V}\right)_{T,P} &= \frac{P}{RT} \\
&= \frac{(0.836\ \text{atm})(101325\ \text{J m}^{-3}\ \text{atm}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.3\ \text{K})} = 34.153\ \text{mol m}^{-3} \\
\varepsilon_n &\approx \Big[(8.003 \times 10^{-6}\ \text{mol Pa}^{-1})^2 \\
&\quad \times [(0.003\ \text{atm})(101325\ \text{Pa atm}^{-1})]^2 \\
&\quad +(-2.273 \times 10^{-3}\ \text{mol K}^{-1})^2(0.2\ \text{K})^2 \\
&\quad +(34.153\ \text{mol m}^{-3})^2(0.00008\ \text{m}^3)^2\Big]^{1/2} \\
\varepsilon_n &\approx [5.918 \times 10^{-6}\ \text{mol}^2 + 2.067 \times 10^{-7}\ \text{mol}^2 \\
&\quad +7.465 \times 10^{-6}\ \text{mol}^2]^{1/2} = 3.7 \times 10^{-3}\ \text{mol} \\
n &= 0.678\ \text{mol} \pm 0.004\ \text{mol}
\end{aligned}$$

3. The van der Waals equation of state is

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

For carbon dioxide, $a = 0.3640$ Pa m^6 mol^{-1} and $b = 4.267 \times 10^{-5}$ m^3 mol^{-1}. Find the pressure of 0.7500 mol of carbon dioxide if $V = 0.0242$ m^3 and $T = 298.15$ K. Find the uncertainty in the pressure if the uncertainty in the volume is 0.00004 m^3 and the uncertainty in the temperature is 0.4 K. Assume that the uncertainty in n is negligible. Find the pressure predicted by the ideal gas equation of state. Compare the difference between the two pressures you calculated and the expected error in the pressure.

$$\begin{aligned}
P &= \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \\
&= \frac{(0.7500\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.1\ \text{K})}{0.0242\ \text{m}^3 - (0.7500\ \text{mol})(4.267 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1})} \\
&\quad - \frac{(0.7500\ \text{mol})^2(0.3640\ \text{Pa m}^6\ \text{mol}^{-1})}{(0.0242\ \text{m}^3)^2} \\
&= 7.6916 \times 10^4\ \text{Pa} - 3.496 \times 10^2\ \text{Pa} = 7.657 \times 10^4\ \text{Pa} \\
\left(\frac{\partial P}{\partial V}\right)_{n,T} &= \frac{nRT}{(V - nb)^2} + \frac{2n^2 a}{V^3} \\
&= \frac{(0.7500\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.1\ \text{K})}{[0.0242\ \text{m}^3 - (0.7500\ \text{mol})(4.267 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1})]^2} \\
&\quad + \frac{2(0.7500\ \text{mol})^2(0.3640\ \text{Pa m}^6\ \text{mol}^{-1})}{(0.0242\ \text{m}^3)^3} \\
&= 3.1836 \times 10^6\ \text{Pa m}^{-3} + 2.889 \times 10^4\ \text{Pa m}^{-3} \\
&= 3.212 \times 10^6\ \text{Pa m}^{-3} \\
\left(\frac{\partial P}{\partial T}\right)_{n,V} &= \frac{nR}{V - nb} \\
&= \frac{(0.7500\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})}{0.0242\ \text{m}^3 - (0.7500\ \text{mol})(4.267 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1})} \\
&= 2.580 \times 10^2\ \text{Pa K}^{-1} \\
\varepsilon_P &= \left[\left(\frac{\partial P}{\partial V}\right)^2 \varepsilon_V^2 + \left(\frac{\partial P}{\partial T}\right)^2 \varepsilon_T^2\right]^{1/2} \\
&= \Big[(3.212 \times 10^6\ \text{Pa m}^{-3})^2(0.00004\ \text{m}^3)^2 \\
&\quad +(2.580 \times 10^2\ \text{Pa K}^{-1})^2(0.4\ \text{K})^2\Big]^{1/2} \\
&= \left[1.651 \times 10^4\ \text{Pa}^2 + 1.065 \times 10^4\ \text{Pa}^2\right]^{1/2} = 1.65 \times 10^2\ \text{Pa} \\
P &= 7.657 \times 10^4\ \text{Pa} \pm 1.65 \times 10^2\ \text{Pa} \\
&= 7.66 \times 10^4\ \text{Pa} \pm 0.02 \times 10^4\ \text{Pa}
\end{aligned}$$

From the ideal gas equation of state

$$\begin{aligned}
P &= \frac{nRT}{V} \\
&= \frac{(0.7500\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.1\ \text{K})}{0.0242\ \text{m}^3} \\
&= 7.681 \times 10^4\ \text{Pa}
\end{aligned}$$

The difference between the value from the van der Waals equation of state and the ideal gas equation of state is

$$\begin{aligned}
\text{difference} &= 7.657 \times 10^4\ \text{Pa} - 7.681 \times 10^4\ \text{Pa} \\
&= -2.4 \times 10^2\ \text{Pa} = -0.024 \times 10^4\ \text{Pa}
\end{aligned}$$

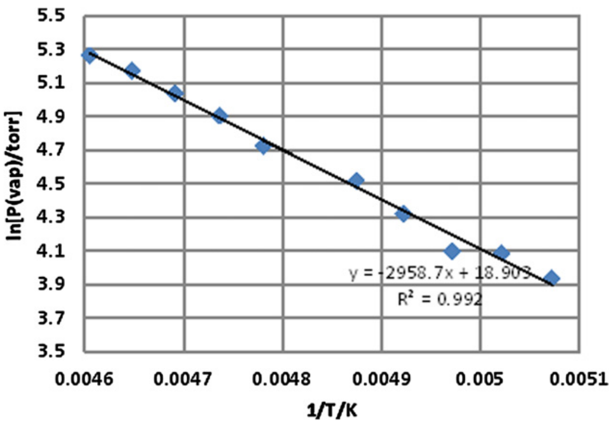
This is roughly the same magnitude as the estimated error.

4. The following is a set of student data on the vapor pressure of liquid ammonia, obtained in a physical chemistry laboratory course.

a. Find the indicated enthalpy change of vaporization.

Temperature/°C	Pressure/torr
−76.0	51.15
−74.0	59.40
−72.0	60.00
−70.0	75.10
−68.0	91.70
−64.0	112.75
−62.0	134.80
−60.0	154.30
−58.0	176.45
−56.0	192.90

Taking the natural logarithms of the pressures and the reciprocals of the absolute temperatures, we carry out the linear least squares fit



$$\ln\left(P_{\text{vap}}/\text{torr}\right) = -2958.7 + 18.903$$

$$\Delta H_{\text{m,vap}} = -Rm = (8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}) \times (2958.7\ \text{K}) = 24600\ \text{J mol}^{-1}$$

b. Ignoring the systematic errors, find the 95% confidence interval for the enthalpy change of vaporization.

$$s_r^2 = \frac{1}{8}\sum_{i=1}^{10} r_1^2 = 0.002113$$

The expected error in the slope is

$$\varepsilon_m = \left(\frac{N}{D}\right)^{1/2} t(\nu,0.05)s_r$$

$$D = NS_{x^2} - S_x^2$$

By calculation

$$S_x = 0.048324$$
$$S_{x^2} = 0.00023376$$

$$\begin{aligned} D &= (10)(0.00023376) - (0.048324)^2 \\ &= 2.39 \times 10^{-6} \\ \varepsilon_m &= \left(\frac{N}{D}\right)^{1/2} t(\nu,0.05)s_r \\ &= \left(\frac{10}{2.39\times 10^{-6}}\right)^{1/2} (2.306)(0.002113)^{1/2} \\ &= 216.8\ \text{K} \\ m &= 2958.7\ \text{K} \pm 217\ \text{K} \\ \Delta H_{\text{vap}} &= 24600\ \text{J mol}^{-1} \pm 1800\ \text{J mol}^{-1} \end{aligned}$$

5. The vibrational contribution to the molar heat capacity of a gas of nonlinear molecules is given in statistical mechanics by the formula

$$C_m(\text{vib}) = R\sum_{i=1}^{3n-6} \frac{u_i^2 e^{-u_i}}{(1-e^{-u_i})^2}$$

where $u_i = h\nu_i/k_BT$. Here ν_i is the frequency of the i th normal mode of vibration, of which there are $3n-6$ if n is the number of nuclei in the molecule, h is Planck's constant, k_B is Boltzmann's constant, R is the ideal gas constant, and T is the absolute temperature. The H_2O molecule has three normal modes. The frequencies are given by

$$\begin{aligned} \nu_1 &= 4.78 \times 10^{13}\ \text{s}^{-1} \pm 0.02 \times 10^{13}\ \text{s}^{-1} \\ \nu_2 &= 1.095 \times 10^{14}\ \text{s}^{-1} \pm 0.004 \times 10^{14}\ \text{s}^{-1} \\ \nu_3 &= 1.126 \times 10^{14}\ \text{s}^{-1} \pm 0.005 \times 10^{14}\ \text{s}^{-1} \end{aligned}$$

Calculate the vibrational contribution to the heat capacity of H_2O vapor at 500.0 K and find the 95% confidence interval. Assume the temperature to be fixed without error.

$$\begin{aligned} u_1 &= \frac{h\nu_1}{k_BT} \\ &= \frac{(6.6260755\times 10^{-34}\ \text{J s})(4.78\times 10^{13}\ \text{s}^{-1})}{(1.3806568\times 10^{-23}\ \text{J K}^{-1})(500.0\ \text{K})} \\ &= 4.588 \\ u_2 &= \frac{h\nu_2}{k_BT} \\ &= \frac{(6.6260755\times 10^{-34}\ \text{J s})(1.095\times 10^{14}\ \text{s}^{-1})}{(1.3806568\times 10^{-23}\ \text{J K}^{-1})(500.0\ \text{K})} \\ &= 10.510 \\ u_3 &= \frac{h\nu_3}{k_BT} \\ &= \frac{(6.6260755\times 10^{-34}\ \text{J s})(1.126\times 10^{14}\ \text{s}^{-1})}{(1.3806568\times 10^{-23}\ \text{J K}^{-1})(500.0\ \text{K})} \\ &= 10.580 \end{aligned}$$

$$C_m(\text{mode 1}) = (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\frac{(4.588)^2e^{-4.588}}{(1-e^{-4.588})^2}$$
$$= 1.817\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$C_m(\text{mode 2}) = (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\frac{(10.51)e^{-10.51}}{(1-e^{-10.51})^2}$$
$$= 0.00238\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$C_m(\text{mode 3}) = (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\frac{(10.58)e^{-10.58}}{(1-e^{-10.58})^2}$$
$$= 0.00224\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$C_m(\text{vib}) = 1.1863\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\varepsilon_1 = \frac{h\varepsilon_{\nu_1}}{k_BT} = \frac{(6.6260755\times10^{-34}\ \text{J s})(0.02\times10^{13}\ \text{s}^{-1})}{(1.3806568\times10^{-23}\ \text{J K}^{-1})(500.0\ \text{K})} = 1.92\times10^{-2}$$
$$\varepsilon_2 = \frac{h\varepsilon_{\nu_2}}{k_BT} = \frac{(6.6260755\times10^{-34}\ \text{J s})(0.004\times10^{14}\ \text{s}^{-1})}{(1.3806568\times10^{-23}\ \text{J K}^{-1})(500.0\ \text{K})} = 3.84\times10^{-2}$$
$$\varepsilon_3 = \frac{h\varepsilon_{\nu_3}}{k_BT} = \frac{(6.6260755\times10^{-34}\ \text{J s})(0.005\times10^{14}\ \text{s}^{-1})}{(1.3806568\times10^{-23}\ \text{J K}^{-1})(500.0\ \text{K})} = 4.80\times10^{-2}$$

$$\frac{\partial C_m}{\partial u_1} = R\left[\frac{2u_1e^{-u1}}{(1-e^{-u_1})^2} - \frac{u_1^2e^{-u_1}}{(1-e^{-u_1})^2} - 2\frac{u_1^2e^{-u_1}}{(1-e^{-u_1})^3}e^{-u_1}\right]$$
$$= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times\left[\frac{2(4.588)e^{-4.588}}{(1-e^{-4.588})^2} - \frac{(4.588)^2e^{-4.588}}{(1-e^{-4.588})^2} - \frac{2(4.588)^2e^{-2(4.588)}}{(1-e^{-4.588})^3}\right]$$
$$= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times[0.09528 - 0.21857 - 0.00449] = -1.025\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\frac{\partial C_m}{\partial u_2} = R\left[\frac{2u_2e^{-u_{i2}}}{(1-e^{-u_2})^2} - \frac{u_i^2e^{-u_2}}{(1-e^{-u_2})^2} - 2\frac{u_2^2e^{-u_2}}{(1-e^{-u_2})^3}e^{-u_2}\right]$$
$$= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times\left[\frac{2(10.51)e^{-10.51}}{(1-e^{-10.51})^2} - \frac{(10.51)^2e^{-10.51}}{(1-e^{-10.51})^2} - \frac{2(10.51)^2e^{-2(10.51)}}{(1-e^{-10.51})^3}\right]$$
$$= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times[0.000573 - 0.00301 - 0.000000164] = -0.02026\ \text{J K}^{-1}\ \text{mol}^{-1}]$$

$$\frac{\partial C_m}{\partial u_3} = R\left[\frac{2u_2e^{-u_{i3}}}{(1-e^{-u_3})^2} - \frac{u_3^2e^{-u_3}}{(1-e^{-u_3})^2} - 2\frac{u_3^2e^{-u_3}}{(1-e^{-u_3})^3}e^{-u_3}\right]$$
$$= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times\left[\frac{2(10.58)e^{-10.58}}{(1-e^{-10.58})^2} - \frac{(10.58)^2e^{-10.58}}{(1-e^{-10.58})^2} - \frac{2(10.58)^2e^{-2(10.58)}}{(1-e^{-10.58})^3}\right]$$
$$= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})[0.0005379 - 0.0028455 - 0.000000145] = -0.01918\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\varepsilon_{C_m} = \left[\left(\frac{\partial C_m}{\partial u_1}\right)^2\varepsilon_1^2 + \left(\frac{\partial C_m}{\partial u_2}\right)^2\varepsilon_2^2 + \left(\frac{\partial C_m}{\partial u_3}\right)^2\varepsilon_3^2\right]^{1/2}$$
$$= [(-1.025\ \text{J K}^{-1}\ \text{mol}^{-1})^2(1.92\times10^{-2})^2 + (-0.02026\ \text{J K}^{-1}\ \text{mol}^{-1})^2(3.84\times10^{-2})^2 + (-0.01918\ \text{J K}^{-1}\ \text{mol}^{-1})^2(4.80\times10^{-2})^2]^{1/2}$$
$$= [3.87\times10^{-4}\ \text{J}^2\ \text{K}^{-2}\ \text{mol}^{-2} + 6.05\times10^{-7}\ \text{J}^2\ \text{K}^{-2}\ \text{mol}^{-2} + 8.48\times10^{-7}\ \text{J}^2\ \text{K}^{-2}\ \text{mol}^{-2}]^{1/2}$$
$$= 0.0197\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$C_m(\text{vib}) = 1.1863\ \text{J K}^{-1}\ \text{mol}^{-1} \pm0.0197\ \text{J K}^{-1}\ \text{mol}^{-1}$$

6. Water rises in a clean glass capillary tube to a height h given by

$$h + \frac{r}{3} = \frac{2\gamma}{\rho gr}$$

where r is the radius of the tube, ρ is the density of water, equal to 998.2 kg m^{-3} at 20 °C, g is the acceleration due to gravity, equal to 9.80 m s^{-2}, h is the height to the bottom of the meniscus, and γ is the surface tension of the water. The term $r/3$ corrects for the liquid above the bottom of the meniscus.

a. If water at 20 °C rises to a height h of 29.6 mm in a tube of radius $r = 0.500$ mm, find the value of the surface tension of water at this temperature.

$$\gamma = \frac{1}{2}\rho gr\left(h + \frac{r}{3}\right) = \frac{1}{2}(998.2\ \text{kg m}^{-3}) \times(9.80\ \text{m s}^{-2})(0.500\times10^{-3}\ \text{m}) \times\left(29.6\times10^{-3}\ \text{m} + \frac{0.500\times10^{-3}\ \text{m}}{3}\right)$$
$$= 0.0728\ \text{kg s}^{-2} = 0.0728\ \text{kg m}^2\ \text{s}^{-2}\ \text{m}^{-2} = 0.0728\ \text{J m}^{-2}$$

b. If the height h is uncertain by 0.4 mm and the radius of the capillary tube is uncertain by 0.02 mm, find the uncertainty in the surface tension.

$$\varepsilon_\gamma = \left[\left(\frac{\partial\gamma}{\partial h}\right)^2\varepsilon_h^2 + \left(\frac{\partial\gamma}{\partial r}\right)^2\varepsilon_r^2\right]^{1/2}$$
$$\left(\frac{\partial\gamma}{\partial h}\right) = \frac{1}{2}\rho gr = \frac{(998.2\ \text{kg m}^{-3})(9.80\ \text{m s}^{-2})(0.500\times10^{-3}\ \text{m})}{2} = 2.446\ \text{J m}^{-3}$$

$$\left(\frac{\partial \gamma}{\partial r}\right) = \frac{1}{6}2\rho g r = \frac{1}{3}\rho g r$$
$$= \frac{(998.2\ \mathrm{kg\ m^{-3}})(9.80\ \mathrm{m\ s^{-2}})(0.500\times 10^{-3}\ \mathrm{m})}{3}$$
$$= 1.630\ \mathrm{J\ m^{-3}}$$

$$\varepsilon_\gamma = \Big[(2.446\ \mathrm{J\ m^{-3}})^2(0.0004\ \mathrm{m})^2 + (1.630\ \mathrm{J\ m^{-3}})^2(0.00002\ \mathrm{m})\Big]^{1/2}$$
$$= [9.6\times 10^{-7}\ \mathrm{J^2\ m^{-6}} + 1.0630\times 10^{-9}\ \mathrm{J^2\ m^{-6}}]^{1/2}$$
$$= 9.8\times 10^{-4}\ \mathrm{J\ m^{-2}}$$
$$\gamma = 0.0728\ \mathrm{J\ m^{-2}} \pm 0.00098\ \mathrm{J\ m^{-2}}$$

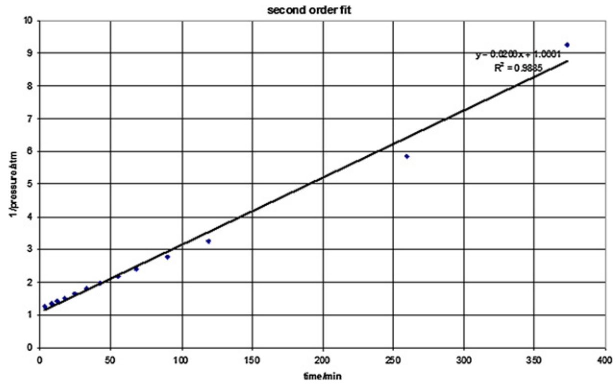
c. The acceleration due to gravity varies with latitude. At the poles of the earth it is equal to 9.83 m $\mathrm{s^{-2}}$. Find the error in the surface tension of water due to using this value rather than 9.80 m $\mathrm{s^{-2}}$, which applies to latitude 38°.

$$\left(\frac{\partial \gamma}{\partial g}\right) = \frac{1}{2}\rho r(h + \frac{r}{3})$$
$$= \frac{1}{2}(998.2\ \mathrm{kg\ m^{-3}})(0.500\times 10^{-3}\ \mathrm{m}) \times \left(29.6\times 10^{-3}\ \mathrm{m} + \frac{0.500\times 10^{-3}\ \mathrm{m}}{3}\right)$$
$$= 0.00743\ \mathrm{kg\ m^{-1}}$$
$$\varepsilon_\gamma = \left|\left(\frac{\partial \gamma}{\partial g}\right)(\varepsilon_g)\right| = \Big|(0.00743\ \mathrm{kg\ m^{-1}}) \times (0.03\ \mathrm{m\ s^{-2}})\Big| = 0.00022\ \mathrm{J\ m^{-2}}$$

7. Vaughan obtained the following data for the dimerization of butadiene at 326 °C.

Time/min	Partial pressure of butadiene/ atm
0	to be deduced
3.25	0.7961
8.02	0.7457
12.18	0.7057
17.30	0.6657
24.55	0.6073
33.00	0.5573
42.50	0.5087
55.08	0.4585
68.05	0.4173
90.05	0.3613
119.00	0.3073
259.50	0.1711
373.00	0.1081

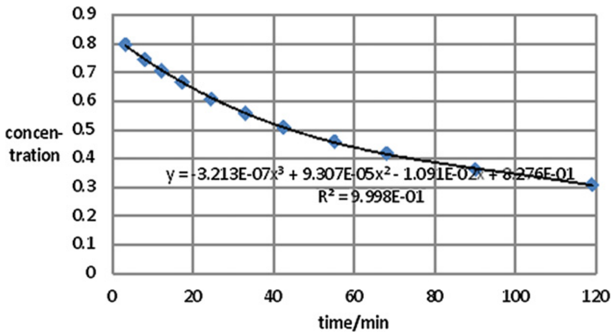
Determine whether the reaction is first, second, or third order. Find the rate constant and its 95% confidence interval, ignoring systematic errors. Find the initial pressure of butadiene. A linear fit of the logarithm of the partial pressure against time shows considerable curvature, with a correlation coefficient squared equal to 0.9609. This is a poor fit. Here is the fit of the reciprocal of the partial pressure against time:



This is a better fit than the first order fit. A fit of the reciprocal of the square of the partial pressure is significantly worse. The reaction is second order. The rate constant is

$$k = \text{slope} = 0.0206\ \mathrm{atm^{-1}\ min^{-1}}$$
$$P(0) = \frac{1}{b} = \frac{1}{1.0664\ \mathrm{atm^{-1}}} = 0.938\ \mathrm{atm}$$

The last two points do not lie close to the line. If one or more of these points were deleted, the fit would be better. If the last point is deleted, a closer fit is obtained, with a correlation coefficient squared equal to 0.9997, a slope equal to 0.0178, and an initial partial pressure equal to 0.837 atm.



8. Make a graph of the partial pressure of butadiene as a function of time, using the data in the previous problem. Find the slope of the tangent line at 24.55 min and deduce the rate constant from it. Compare with the result from the previous problem.

Here is the graph, with a fit to a third-degree polynomial. To find the derivative, we differentiate the polynomial:

$$\frac{dP}{dt} = -9.639 \times 10^{-7}t^2 +1.8614 \times 10^{-4}t - 0.01091$$

$$\left.\frac{dP}{dt}\right|_{t=24.55} = -0.00692 \text{ atm min}^{-1}$$

$$\frac{dP}{dt} = -kc^2$$

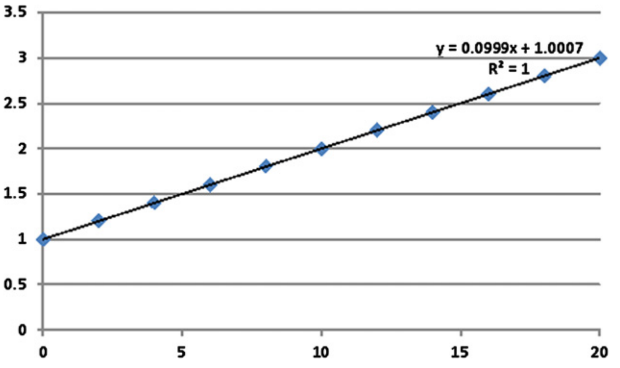
$$k = -\frac{dP/dt}{P^2} = \frac{0.00692 \text{ atm min}^{-1}}{(0.6073 \text{ atm})^2} = 0.0188 \text{ atm}^{-1} \text{ min}^{-1}$$

This value is smaller than the value in the previous problem by 9%, but is larger than the value obtained by deleting the last two data points by 8%.

9. The following are (contrived) data for a chemical reaction of one substances.

Time/min	Concentration/mol l^{-1}
0	1.000
2	0.832
4	0.714
6	0.626
8	0.555
10	0.501
12	0.454
14	0.417
16	0.384
18	0.357
20	0.334

a. Assume that there is no appreciable back reaction and determine the order of the reaction and the value of the rate constant. A linear fit of the natural logarithm of the concentration against the time showed a general curvature and a correlation coefficient squared equal to 0.977. A linear fit of the reciprocal of the concentration against the time gave the following fit:



This close fit indicates that the reaction is second order. The slope is equal to the rate constant, so that

$$k = 0.0999 \text{ l mol}^{-1} \text{ min}^{-1}$$

b. Find the expected error in the rate constant at the 95% confidence level. The sum of the squares of the residuals is equal to 9.08×10^{-5}. The square of the standard deviation of the residuals is

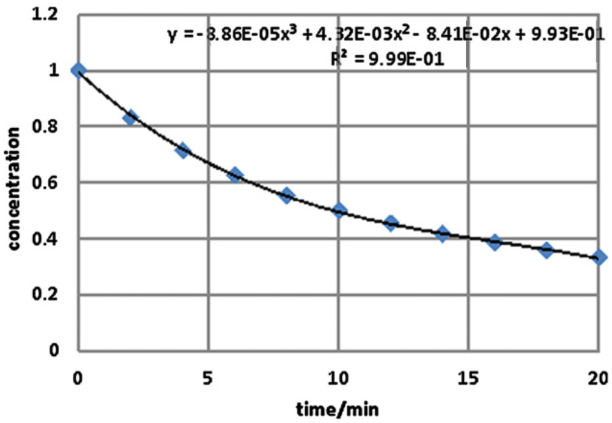
$$s_r^2 = \frac{1}{9}(9.08 \times 10^{-5}) = 1.009 \times 10^{-5}$$

$$D = NS_{x^2} - S_x^2 = 11(1540) - (110)^2 = 1.694 \times 10^4 - 1.21 \times 10^4 = 4.84 \times 10^3$$

$$\varepsilon_m = \left(\frac{N}{D}\right)^{1/2} t(\nu,0.05)s_r = \left(\frac{11}{4.84 \times 10^3}\right)^{1/2} \times (2.262)(1.009 \times 10^{-5}) = 3.4 \times 10^{-4} \text{ l mol}^{-1} \text{ min}^{-1}$$

$$k = 0.0999 \text{ l mol}^{-1} \text{ min}^{-1} \pm 0.0003 \text{ l mol}^{-1} \text{ min}^{-1}$$

c. Fit the raw data to a third-degree polynomial and determine the value of the rate constant from the slope at $t = 10.00$ min. Here is the fit:



$$c = -8.86 \times 10^{-5}t^3 + 4.32 \times 10^{-3}t^2 - 8.41 \times 10^{-2}t + 0.993$$

$$\frac{dc}{dt} = -2.66 \times 10^{-4}t^2 + 8.64 \times 10^{-3}t - 8.41 \times 10^{-2}$$

At time $t = 10.00$ min

$$\frac{dc}{dt} = -0.0243$$

$$\frac{dc}{dt} = -kc^2$$

$$k = -\frac{dc/dt}{c^2} = \frac{0.0243 \text{ mol l}^{-1} \text{ min}^{-1}}{(0.501 \text{ mol l}^{-1})^2} = 0.0968 \text{ l mol}^{-1} \text{ min}^{-1}$$

The value from the least-squares fit is probably more reliable.

10. If a capacitor of capacitance C is discharged through a resistor of resistance R the voltage on the capacitor follows the formula

$$V(t) = V(0)e^{-t/RC}$$

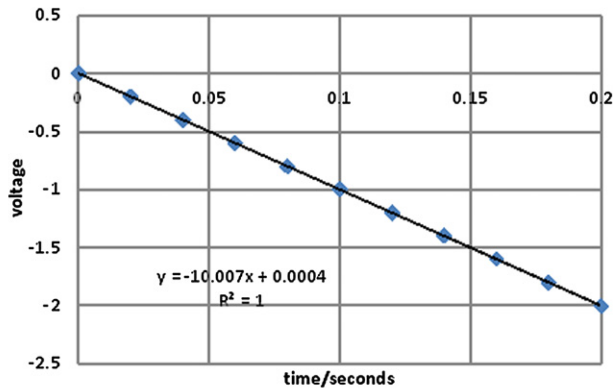
The following are data on the voltage as a function of time for the discharge of a capacitor through a resistance of 102 kΩ.

t/s	V/volt
0.00	1.00
0.020	0.819
0.040	0.670
0.060	0.549
0.080	0.449
0.100	0.368
0.120	0.301
0.140	0.247
0.160	0.202
0.180	0.165
0.200	0.135

Find the capacitance and its expected error.

$$\ln\left(\frac{V(t)}{V(0)}\right) = -\frac{t}{RC}$$

Here is the linear fit of $\ln[V(t)/V(0)]$ against time



$$C = -\frac{m}{R} = \frac{10.007 \text{ s}^{-1}}{102000 \ \Omega} = 9.81 \times 10^{-5} \text{ F} = 98.1 \ \mu\text{F}$$

The sum of the squares of the residuals is equal to 1.10017×10^{-5}

$$s_r^2 = \frac{1}{9}(1.10017 \times 10^{-5}) = 1.222 \times 10^{-6}$$

$$s_r = \sqrt{1.222 \times 10^{-6}} = 1.105 \times 10^{-3}$$

$$D = NS_{x^2} - S_x^2 = 12(0.154) - (1.100)^2 = 1.848 - 1.2100 = 0.638$$

The expected error in the slope is given by

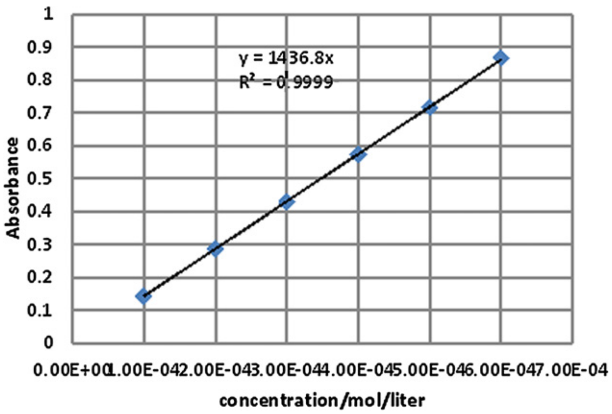
$$\varepsilon_m = \left(\frac{N}{D}\right)^{1/2} t(9{,}0.05)s_r = \left(\frac{11}{0.638}\right)^{1/2}$$
$$\times(2.262)(1.105\times10^{-3}) = 1.04\times10^{-2}$$
$$m = -10.007\ \mathrm{s}^{-1} \pm 0.0104\ \mathrm{s}^{-1}$$
$$C = \frac{10.007\ \mathrm{s}^{-1}}{102000\ \Omega} \pm \frac{0.0104\ \mathrm{s}^{-1}}{102000\ \Omega}$$
$$= 9.81\times10^{-5}\ \mathrm{F} \pm 1.0\times10^{-7}\ \mathrm{F}$$
$$= 98.1\ \mu\mathrm{F} \pm 0.1\ \mu\mathrm{F}$$

11. The Bouguer–Beer law (sometimes called the Lambert–Beer law or Beer's law) states that $A = abc$, where A is the of a solution, defined as $\log_{10}(I_0/I)$ where I_0 is the incident intensity of light at the appropriate wavelength and I is the transmitted intensity; b is the length of the cell through which the light passes; and c is the concentration of the absorbing substance. The coefficient a is called the molar absorptivity if the concentration is in moles per liter. The following is a set of data for the absorbance of a set of solutions of disodium fumarate at a wavelength of 250 nm.

A	0.1425	0.2865	0.4280	0.5725	0.7160	0.8575
c (mol l^{-1})	1.00×10^{-4}	2.00×10^{-4}	3.00×10^{-4}	4.00×10^{-4}	5.00×10^{-4}	6.00×10^{-4}

Using a linear least-squares fit with intercept set equal to zero, find the value of the absorptivity a if $b = 1.000$ cm. For comparison, carry out the fit without specifying zero intercept.

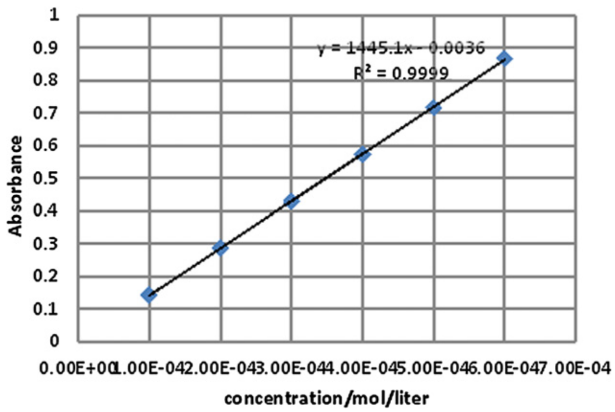
Here is the fit with zero intercept specified:



$$A = abc$$

$$\text{slope} = m = ab = 1436.8\ \mathrm{l\ mol^{-1}}$$
$$a = \frac{m}{b} = \frac{1436.8}{1.000\ \mathrm{cm}} = 1437\ \mathrm{l\ mol^{-1}\ cm^{-1}}$$

Here is the fit with no intercept value specified:



$$a = \frac{m}{b} = \frac{1445.1}{1.000\ \mathrm{cm}} = 1445\ \mathrm{l\ mol^{-1}\ cm^{-1}}$$

The value from the fit with zero intercept specified is probably more reliable.

$$a = 1437\ \mathrm{l\ mol^{-1}\ cm^{-1}}$$