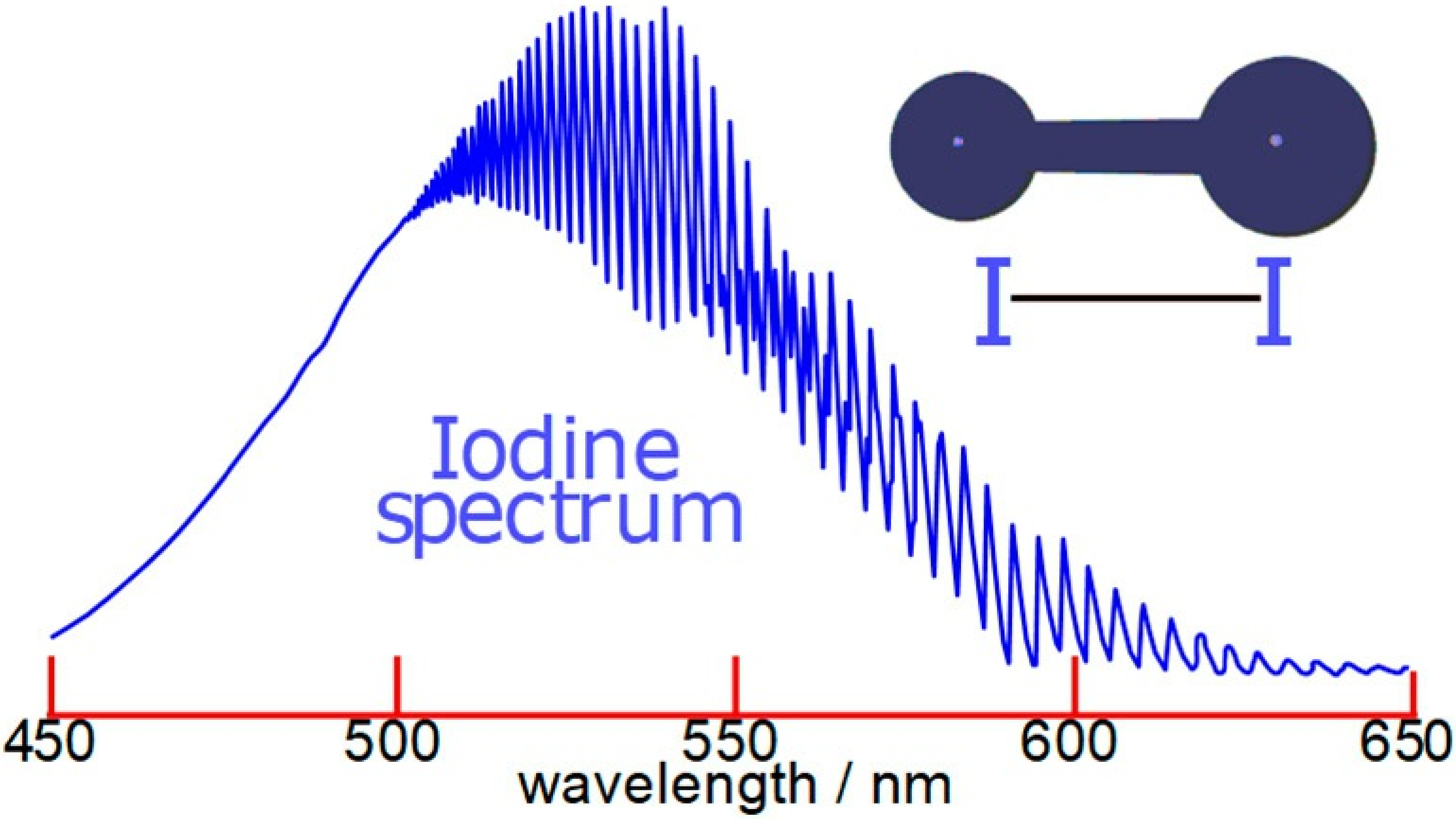

J. E. Parker

Intermediate Maths for Chemists

Chemistry Maths 2

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J. E. PARKER

INTERMEDIATE MATHS FOR CHEMISTS

CHEMISTRY MATHS 2

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I was pleased to respond to bookboon.com to write a textbook (which is split into 3 more manageable books, *Introductory Maths for Chemists*, *Intermediate Maths for Chemists*, and *Advanced Maths for Chemists* which should be studied in sequence) that would help chemistry students survive and enjoy the maths required for a chemistry degree. I developed and presented tutorials on maths to our first year chemistry students over several years at Heriot-Watt University, Edinburgh, Scotland. This formed the basis for these workbooks. I would like to thank the staff of Heriot-Watt University for their help; and thank the students who 'suffered' these tutorials, hopefully they helped them with their degrees and later careers. Most of all I would like to thank my wife Jennifer for her encouragement and help over many years.

I shall be delighted to hear from readers who have comments and suggestions to make, please email me. So that I can respond in the most helpful manner I will need your full name, your University, the name of your degree and which level and year of the degree you are studying. I hope you find these textbooks helpful and I wish you good luck with your studies.

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ABOUT THE AUTHOR

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The author, John Parker, has 39 years experience of teaching chemists, biologists, pharmacists, chemical engineers and other engineers at Heriot-Watt University Edinburgh. The author's research interests from 1966 onwards are physical and analytical chemistry, especially chemical kinetics, spectroscopy, statistical mechanics, quantum mechanics, computational chemistry and the use of mass spectrometric techniques to study single-collision reactions. The author's teaching was mostly in physical chemistry for years 1 to 4 of BSc and MChem and PhD students using combinations of lectures, tutorials and lab classes. During this time the author developed the content and taught maths to first year chemists for several years. The author believes that maths must be put into a chemistry context for the students to grasp its significance, usefulness and its application in science and engineering.

1 WEEK 1: CHEMISTRY AND DIFFERENTIATION 1

1.1 INTRODUCTION

I have deliberately repeated the introductory sections of *Introductory Maths for Chemists* (Parker 2018) here for your convenience. I suggest you look through this introduction rather than jumping to Section 1.2.

The three books; *Introductory Maths for Chemists,* (Parker 2018), *Intermediate Maths for Chemists* (Parker 2012, new edition due 2019), and *Advanced Maths for Chemists* (Parker 2013, new edition due in 2019) are tutorial workbooks intended for first year undergraduates taking a degree in chemistry, chemical engineering, chemical physics, molecular biology, biochemistry, or biology. From now on I will be using the term ‘chemistry’ as a shorthand to cover chemical engineering, chemical physics, molecular biology, biochemistry, or biology as well as chemistry itself. The texts may also be very useful for final year school or college students prior to them starting an undergraduate degree and also to their chemistry teachers and lecturers. The text is published as three books in order to reduce file size and make handling on a laptop or tablet much easier. *Introductory Maths for Chemists* roughly covers the first 8 weeks of semester 1; *Intermediate Maths for Chemists* the remainder of semester 1 and the beginning of semester 2; and *Advanced Maths for Chemists* the rest of semester 2. They each have chapters named as Week 1, Week 2… this is purely to help you self-pace your work on a weekly basis.

Go through the questions and work out the solution yourself on paper then check your solution. Full solutions are given to show you the method of solving the problem. Initially the solutions give most of the steps but as you progress through the workbook the explanations become less detailed. When you do finally cover the chemistry involved in the examples during your chemistry degree you won’t be blinded or scared by the maths as by then you will be happy playing around with equations and graphs.

One final and important comment, a common mistake of many students is thinking you need to memorize all the equations you come across in any area of the subject. This is impossible and I know that I, or any other member of staff, can’t remember them all. There are a very small number of equations that become familiar simply by usage and which you remember without really trying. All the rest come from being able to apply your maths to this small number of familiar equations or to the equations supplied in an exam or from a textbook and this enables you to get to your target.

1.1.1 WHY DO CHEMISTS HAVE TO DO MATHS?

Maths is a convenient and fast shorthand language that summarizes the details of a particular topic of chemistry. It is the language of chemistry, it is also the underlying language of all the sciences and engineering. So we won't be able to become really fluent in chemistry, or other science subjects, or engineering until we understand the 'shorthand' language of maths.

1.1.2 HOW THE WORKBOOK IS STRUCTURED

At the beginning of your university chemistry degree you may find that many of the chemistry examples used in this workbook have not yet been covered in your chemistry course. Don't worry. We are trying to understand the maths at the moment more than the chemistry, and the chemistry details will come later as you progress in your degree. Just treat these examples as maths examples, which is what they are, and solve the maths. The chemistry will add meaning to the maths, which otherwise can be a bit abstract.

1.1.3 PHYSICAL QUANTITIES

In your maths lessons in school or college the variables used were probably x and y and angles θ or α as these are the general symbols used by mathematicians. But in science and engineering all the variables we use are physical quantities, such as mass, length, time, force, work, enthalpy, entropy, and so on. These physical quantities usually have a conventional symbol agreed by usage of the international community of scientists, for example, IUPAC the 'International Union of Pure and Applied Chemistry' and IUPAP for physics. These symbols are used in the maths equations describing the phenomenon of interest. A few examples of the symbols used for physical quantities are m for mass, c for the velocity of light and E for energy. These come together in the equation that everyone has met, $E = mc^2$. In maths this is equivalent to $y = ax^2$ which could apply to many situations, however, $E = mc^2$ only applies to the specific process of conversion of a physical mass into energy. So this book will get you accustomed to using maths in the real world of manipulating equations made up of physical quantities written in the accepted scientific way.

$$\overbrace{c}^{\text{physical quantity}} = \overbrace{2.9979\times10^{8}}^{\text{pure number}}\ \overbrace{\text{m s}^{-1}}^{\text{units}}$$

Example of a physical quantity

A physical quantity may be a variable or a constant they consist of two parts; a pure number (which in scientific notation may includes a multiplier of ten raised to a power) and units. The pure number and the units are inseparable. An example would be $c = 2.9979\times10^{8}$ m s^{-1} where c is the symbol for the velocity of light. In order to clearly distinguish the three parts of the above equation, the symbol for physical quantity is written in italics (sloping) font and the number and the symbols for the units are in roman (upright) font with a space between the number and the units. The degree Celsius has the symbol °C, so the space goes between the number and the unit as in 25 °C. Don't worry too much about hand written material but for typed material it should be typed correctly.

Some units are named after people such as Sir Isaac Newton or Lord Kelvin. When we refer to the person then their name has an initial capital letter, Newton or Kelvin, but the unit name is all lower case, newton or kelvin. The unit symbol is an initial capital of one or sometimes two letters (N for newton and K for kelvin). The use of initial capital for units has a few exception for historical reasons eg the second (s), the kilogram (kg), metre (m), centimetre (cm), and degree Celsius (°C). When we substitute a physical quantity for its symbol in an equation we must substitute both the number and the units into the equation, they are inseparable, they go together like the two sides of a piece of paper.

1.1.4 LINEAR OR STRAIGHT LINE GRAPHS

Straight line graphs are important in science. Linear graphs are particularly useful as being strong evidence that the maths equation really does model the chemistry. Linear graphs are much easier to use in this way than curved graphs. They also allow you to spot any 'rogue' or outlying experimental data points which can be checked back in the lab.

$y = mx + c$ Equation of a straight line graph

The two variables are x and y. The gradient of the line (how quickly y increases or decreases as x is increased) is m, and c is the intercept on the y-axis (the offset that y starts with when x = 0).

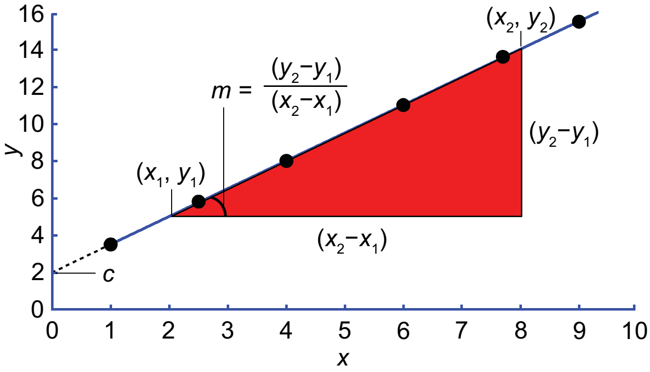

Figure 1.1: intercept and gradient for a linear graph.

The vertical axis in Fig. 1.1 is the y-axis and the horizontal axis is the x-axis. Whatever names are used for the variables in a particular situation, we should always say 'plotting y against x' where the variable names are used instead of y and x so the graph will always have an unambiguous meaning.

Graph axes, table headings, and the table data arethe physical quantities *divided by* the units and any numerical multiplier. Graph axes, table headings, and the table data are *small* pure numbers.

Where possible is it best to use a spreadsheet to plot the graph and find the equation of the line, both linear and non-linear least squares curve fitting are discussed in *Advanced Maths for Chemists* (Parker 2013, new edition 2019). But you also need to be able to carry out the process by hand on graph paper, perhaps in an exam where computers, phones, and graphic calculators are normally not allowed except for some 'open-book' type of exams, so practice with some of these tutorial questions! Once you have used your judgement to draw the best straight line eg by using a transparent ruler then the equation of the best straight line is found as follows. Using the line itself, but not the data points (otherwise what was the point of drawing a best straight line) pick two positions on the line near the left hand side and near the right hand side of Fig. 1.1 $(x_1, y_1) = (2, 5)$ and $(x_2, y_2) = (8, 14)$.

(1) $5 = m2 + c$ (2) $14 = m8 + c$

(3) $9 = m6$ $m = 1.5$ (4) $19 = m10 + 2c$ The equation of a linear graph

(5) $19 = 1.5\times10 + 2c$ $c = 2$ (6) $y = 1.5x + 2.0$

The two points selected on the line give us two simultaneous equations, these are (1) and (2). Subtraction of (1) from (2) gives the gradient (3) as $m = 1.5$. Addition of (1) and (2) gives (4) into which we substitute $m = 1.5$ and find the intercept (5) as $c = 2$. The equation for the best straight line (6) is $y = 1.5x + 2$.

Quite often the data is such that the graph has a very large intercept, not like Fig. 1.1, then it is necessary to plot the graph with the intersection of the axes not at the origin (0, 0) but at a more convenient point. Also the scale of the axes must be adjusted so the data points occupy a reasonably large area (about half an A4 page in portrait mode is a useful size for a lab notebook). Then the only way to obtain gradients and intercepts is by finding the equation of the line as in the above method or preferably with a spreadsheet.

Graphs should be scaled so the data points fill most of the available space. The axes may not intersect at (0, 0) and the origin might not be visible on the graph. Do *not* extrapolate but find the equation of the best fit straight line.

In chemistry often the equation that models the chemical behaviour is not a straight line function. Then maths may be used to rearrange the equation to obtain a linear function. A linear plot is supporting evidence that the model (a mathematical representation or theory of a phenomenon) agrees with the experimental data (the facts). This is the first test of a scientific theory, the second test is that it predicts further experiments to test the theory or model.

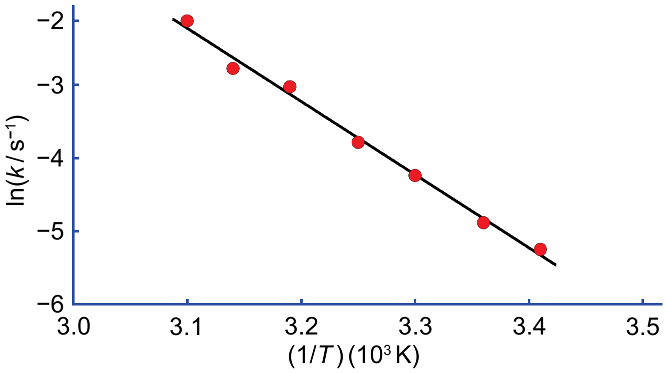

Figure 1.2: a typical Arrhenius plot.

Fig. 1.2 is a typical plot of data from a rearranged Arrhenius equation, which we will discuss later in the book. The rearranged Arrhenius equation is a plot of the natural log of the rate constant against the reciprocal of temperature. Notice how the axes are labelled as small pure numbers. The axes scales fit all the data and the intersection of the axes is a long way from the origin (0, 0).

Perhaps a little confusing at first sight, is the fact that the x-axis in Fig. 1.2 is $1/T$ and it is multiplied and not divided by a numerical factor and units. As some people have problems with this type of reciprocal labelling I have shown the steps from (7) to (12) below, using T = 300 K as an example for our x-axis labelling.

$$(7)\quad T = 300\ \mathrm{K} \qquad (8)\quad \frac{1}{T} = \frac{1}{300\ \mathrm{K}} \qquad (9)\quad \frac{1}{T} = 0.003333\ \mathrm{K}^{-1}$$

$$(10)\quad \frac{1}{T} = 3.333\times10^{-3}\ \mathrm{K}^{-1} \qquad (11)\quad \frac{1/T}{10^{-3}\ \mathrm{K}^{-1}} = 3.333 \qquad (12)\quad (1/T)(10^{3}\ \mathrm{K}) = 3.333$$

The axis are clearer plotted as small numbers hence the division by the multiplier in (11). The x-axis is better for later processing of results when written as $(1/T)(10^3\ \mathrm{K}) = 3.333$ as in (12) rather than (11).

$$(13)\quad \overbrace{\ln\left(k/\mathrm{s}^{-1}\right)}^{y} = \overbrace{-9.98\left(10^{3}\ \mathrm{K}\right)}^{m}\overbrace{\left(1/T\right)}^{x} + \overbrace{28.7}^{c} \qquad (14)\quad m = -9.98\times10^{3}\ \mathrm{K} = -\frac{E_{\mathrm{a}}}{R}$$

$$(15)\quad E_{\mathrm{a}} = \left(9.98\times10^{3}\ \mathrm{K}\right)\left(8.314\ \mathrm{J\ K^{-1}mol^{-1}}\right) \qquad (16)\quad E_{\mathrm{a}} = 82.97\times10^{3}\ \mathrm{J\ mol^{-1}}$$

$$(17)\quad E_{\mathrm{a}} = 82.97\ \mathrm{kJ\ mol^{-1}}$$

The best-fit straight line equation of Fig. 1.2 is (13). In Section 3.1.1 on logs we find that logs must always be pure numbers. So in $\ln(k/\mathrm{s}^{-1})$ the physical quantity and the units in the brackets cannot be separated out and still remain a log. The x-axis is written as $(1/T)(10^3\ \mathrm{K})$ so that we can plot a small pure number however the gradient m is a physical quantity with a multiplier and units (14). We will discover later on that the gradient (14) of the Arrhenius equation equals $-E_\mathrm{a}/R$ where R is the gas constant and E_a is the activation energy. So (15) cancelling out the negatives and taking the gas constant over to the right we obtain the activation energy E_a in (16) and in (17) it is written with the conventional units of kJ mol^{-1}.

$$(18)\quad c = \ln\left(A/\mathrm{s}^{-1}\right) = 28.7 \qquad (19)\quad A/\mathrm{s}^{-1} = \exp(28.7)$$

$$(20)\quad A/\mathrm{s}^{-1} = 2.91\times10^{12} \qquad (21)\quad A = 2.91\times10^{12}\ \mathrm{s}^{-1}$$

From the equation of the best-fit straight line for Fig. 1.2, the intercept is $c = 28.7$ in (18). From the rearranged Arrhenius equation the intercept is also $c = \ln(A/\mathrm{s}^{-1})$. Don't worry if at the moment you are unsure of logs and antilogs as we will cover all of that area in Week 3 of this book. In (19) we take the antilog of the intercept. In (20) now there are no longer any logs so we may now take the units over to the right hand side to give (21) the pre-exponential factor with its correct units.

The gas constant R = 8.3145 J K^{-1} mol^{-1} appears in many situations in science that don't involve ideal gases! Its name is purely historical and the reason for its appearance is that the gas constant is a 'disguise' for the much more fundamental Boltzmann's constant $R = N_A k_B$ (N_A is Avogadro's constant). Boltzmann's constant k_B applies to individual atoms or molecules whether they be a gas, liquid, or a solid. The gas constant is just Boltzmann's constant for a mole of the atoms or molecules whether they be gas, liquid, or solid.

1.1.5 SUGGESTED TEXTBOOKS

Intermediate Maths for Chemists may be used with any maths textbook, however, the students and I found the textbook (Stroud and Booth 2013) very useful. Despite its name of *Engineering Mathematics* Stroud and Booth's book covers all the maths needed by all the sciences and engineering subjects. *Intermediate Maths for Chemists* gives chemical examples of the maths concepts. If you want to look up any first year chemistry then any general chemistry textbook is useful but the textbook (Blackman, Bottle, Schmid, Mocerino and Wille 2015) is excellent. For later on in your course the following textbooks have many examples of the interplay between chemistry and maths mainly in physical chemistry: Atkins and de Paula and Keeler 2017, and Atkins and de Paula 2016, and Levine 2009.

I use LibreOffice Writer, Calc spreadsheet, Draw, and Math for maths equations (LibreOffice 2019). However to find the areas under a curve between two points, tangents, normals, first and second differentials of a curve I use Graph 4.4.2 (Johansen 2019). For visualizing molecules I use Jmol (Jmol 2019). These three software packages are free.

1.2 WEEK 1 TUTORIAL QUESTIONS

Chemistry and differentiation 1 will take both weeks 1 and 2. There are five maths topics to be considered with respect to differentiation and the tutorial questions reflect some of the most common uses that chemistry makes of the five topics of differentiation. The topics are: the product rule, the quotient rule, the chain rule, parametric differentiation, and the Taylor and Maclaurin series expansions of simple functions.

The Taylor series represents a curve or a function as a sum of terms where each term is calculated from the next higher derivative at a single point of the curve. Fig. 1.3 shows the function $f(x)$ at the point on the curve where $x = a$ that is the curve at $f(a)$. The Taylor series expansion for the curve at $f(a)$ is shown below.

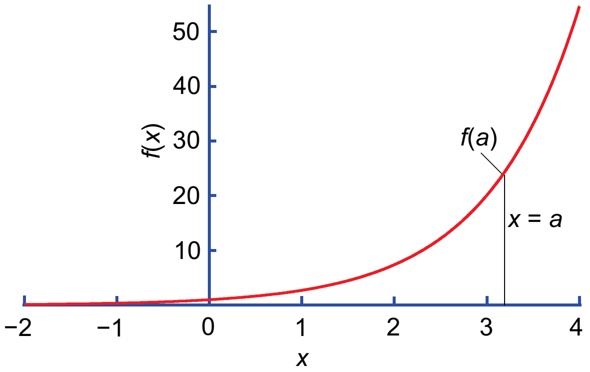

Figure 1.3: Taylor series.

$$f(x) = f(a) + (x-a)\frac{\mathrm{d}f(a)}{\mathrm{d}x} + \frac{(x-a)^2}{2!}\frac{\mathrm{d}^2 f(a)}{\mathrm{d}x^2} + \frac{(x-a)^3}{3!}\frac{\mathrm{d}^3 f(a)}{\mathrm{d}x^3} + \cdots \quad \text{Taylor series}$$

If the point of the expansion is at $a = 0$ then the series is called a Maclaurin series, which is a specific version of the more general Taylor series.

$$f(x) = f(0) + x\frac{\mathrm{d}f(0)}{\mathrm{d}x} + \frac{x^2}{2!}\frac{\mathrm{d}^2 f(0)}{\mathrm{d}x^2} + \frac{x^3}{3!}\frac{\mathrm{d}^3 f(0)}{\mathrm{d}x^3} + \ldots \quad \text{Maclaurin series}$$

1.2.1 QUESTION 1: QUANTUM MECHANICS IN TWO-DIMENSIONS

Consider a particle of mass m confined by walls of infinite potential energy to a surface and the particle is trapped in a two-dimensional box. A particle is the general name for a molecule, atom, electron, or ion.

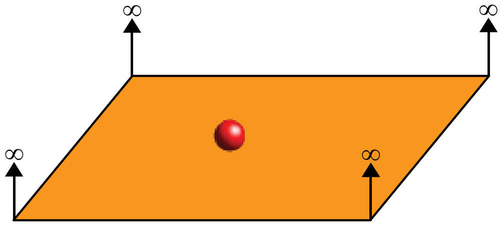

Figure 1.4: a particle confined on a surface of atomic dimensions.

If the size of the two sides of the box are small and of atomic dimensions then quantum effects will dominate (section 4.2.1). The walls of the surface are of 'infinite' potential energy and this confines the particle. The particle might be an electron confined in a quantum well on a semiconductor surface which is the chemistry responsible for some solid state display devices. Fig. 1.5 shows the wavefunction ψ (psi) of the four lowest energy levels of a particle confined in a square two-dimensional box with $L_X = 1$ and $L_Y = 1$.

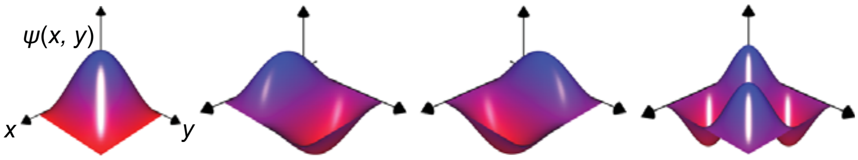

Figure 1.5: left to right n_X and n_Y: 1,1; 1,2; 2,1; and 2,2.

The energy levels E for the particle depends on the lengths of the two sides of the box, L_X and L_Y and the quantum numbers associated with these two directions n_X and n_Y. The quantum numbers may each independently take the integer values $n_X = 1, 2, 3, \ldots$ and $n_Y = 1, 2, 3, \ldots$ and h is Planck's constant.

$$E = \left(\frac{n_X^2}{L_X^2} + \frac{n_Y^2}{L_Y^2}\right)\frac{h^2}{8\,m} \quad \text{Particle in a two-dimensional box}$$

The maths of electrons trapped in two-dimensional boxes has applications in surface chemistry and surface physics. Devices such as quantum well lasers which are laser diodes and have enabled the internet to spread using fibre-optics with high speeds of data transfer. The typical lifetime of quantum well lasers is now about 25 years. Another application is quantum dots which relies on them fluorescing when exposed to light. These fluorescent quantum dots are used for medical imaging of lymph nodes to look for cancer cells by shining light on the outside of the lymph node. Designing and manufacturing these devices (as well as others) involves a combination of chemistry, maths, and physics.

Keeping the energy E of the particle constant, determine $\mathrm{d}L_X/\mathrm{d}L_Y$ where L_X is an unknown function of L_Y. This is an example of 'implicit differentiation', *i.e.* find $\mathrm{d}E/\mathrm{d}L_Y$ and set this equal to zero as we know the energy is constant. The resulting expression may then be rearranged using the 'separation of variables of a derivative' and the 'chain rule' to find a solution for $\mathrm{d}L_X/\mathrm{d}L_Y$.

Jump to Solution 1 (see page 19)

1.2.2 QUESTION 2: ELECTRONS IN ATOMIC ORBITALS

The probability of finding an electron of an atom anywhere within an infinitesimal thin spherical 'shell' of radius r from the nucleus and thickness $\mathrm{d}r$ is given by the radial distribution function P.

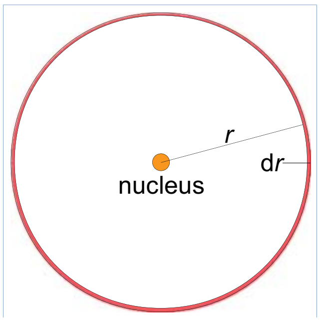

Figure 1.6: cross-section through a spherical shell.

$$P = \frac{4}{a_0^3} r^2 \,\mathrm{e}^{-2r/a_0}$$ Radial distribution function for a 1s H-atom electron

Where a_0 is a constant called the Bohr radius. What is the radius for maximum probability for the 1s electron? In order to calculate the maximum value of P we need to find the differential $\mathrm{d}P/\mathrm{d}r$ using the product rule for differentiation and set $\mathrm{d}P/\mathrm{d}r$ equal to zero.

$$\frac{\mathrm{d}(uv)}{\mathrm{d}x} = u\frac{\mathrm{d}v}{\mathrm{d}x} + v\frac{\mathrm{d}u}{\mathrm{d}x}$$ Product rule for differentiation

Jump to Solution 2 (see page 20)

1.2.3 QUESTION 3: VIBRATION OF MOLECULAR BONDS AND HEAT CAPACITY

When we heat a monatomic gas at constant volume the temperature increases due to the increase in translational energy. But when we supply the same amount of heat to a gaseous diatomic molecules at constant volume the temperature increases but not by as much as that for the monatomic gas. The difference has gone into exciting the quantum energy levels of rotation and vibration (but not electronic levels as the electronic energy gaps are too large to be excited by moderate heating). So heat capacity measurements C_V are classical lab experiments that we can carry out relatively easily that gives us an insight into the internal energy of the molecules and of the quantized energy levels of the molecules. Fig. 1.7 shows at constant volume, that heating the gas alters the population of the molecules on the quantum level ladder towards higher energy levels.

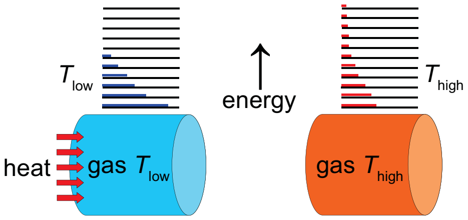

Figure 1.7: heating a gas at constant volume.

The contribution to the internal energy arising from the molecular vibrations U^{V} (superscript V for vibration) of n moles of diatomic molecules (assuming the vibrations are harmonic) is as follows.

$$U^{\mathrm{V}} = n N_{\mathrm{A}} h c \bar{\upsilon} \frac{\mathrm{e}^{-hc\bar{\upsilon}\beta}}{1-\mathrm{e}^{-hc\bar{\upsilon}\beta}}$$

Vibrational internal energy of diatomic molecules

Where the thermodynamic beta β is equal to $1/k_{\mathrm{B}}T$ where k_{B} is Boltzmann's constant $k_{\mathrm{B}} = R/N_{\mathrm{A}}$ with R the gas constant. N_{A} is Avogadro's constant and T is the absolute temperature. The bond vibrational wavenumber is $\bar{\upsilon}$ with h Planck's constant and c the velocity of light.

Note that $nN_{\mathrm{A}}hc\bar{\upsilon}$ are all constants for n moles of a given molecule. First, calculate the differential $\mathrm{d}U^{V}/\mathrm{d}\beta$ noting that to differentiate the quotient of two terms (u/v) we use the quotient rule of differentiation. Don't confuse v (vee) with $\bar{\upsilon}$ (nu bar).

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{u}{v}\right) = \frac{v\left(\frac{\mathrm{d}u}{\mathrm{d}x}\right) - u\left(\frac{\mathrm{d}v}{\mathrm{d}x}\right)}{v^2}$$

Quotient rule for differentiation

Secondly, substitute your expression for $\mathrm{d}U^{V}/\mathrm{d}\beta$ into the equation for the vibrational heat capacity at constant volume C_V^{V} for a collection of vibrating molecules.

$$C_V^{\mathrm{V}} = -k_{\mathrm{B}}\beta^2 \frac{\mathrm{d}U^{\mathrm{V}}}{\mathrm{d}\beta}$$

Vibrational heat capacity for SHO diatomic molecules

Jump to Solution 3 (see page 23)

1.3 WEEK 1 TUTORIAL SOLUTIONS

1.3.1 SOLUTION 1: QUANTUM MECHANICS IN TWO DIMENSIONS

$$(1)\quad \frac{\mathrm{d}E}{\mathrm{d}L_Y} = \frac{h^2}{8m}\frac{\mathrm{d}}{\mathrm{d}L_Y}\left(\frac{n_X^2}{L_X^2}+\frac{n_Y^2}{L_Y^2}\right) \qquad (2)\quad \frac{\mathrm{d}E}{\mathrm{d}L_Y} = \frac{h^2}{8m}\left(\frac{\mathrm{d}}{\mathrm{d}L_Y}\left(\frac{n_X^2}{L_X^2}\right)+\frac{\mathrm{d}}{\mathrm{d}L_Y}\left(\frac{n_Y^2}{L_Y^2}\right)\right)$$

$$(3)\quad \frac{\mathrm{d}}{\mathrm{d}L_Y}\left(\frac{n_Y^2}{L_Y^2}\right) = -\frac{2n_Y^2}{L_Y^3} \qquad (4)\quad \frac{\mathrm{d}E}{\mathrm{d}L_Y} = \frac{h^2}{8m}\left(\frac{\mathrm{d}}{\mathrm{d}L_Y}\left(\frac{n_X^2}{L_X^2}\right)-\frac{2n_Y^2}{L_Y^3}\right)$$

(1) Using implicit differentiation we differentiate the energy E with respect to the distance L_Y because the question asks for $\mathrm{d}L_X/\mathrm{d}L_Y$ with $\mathrm{d}L_Y$ as the denominator. As $h^2/8m$ is constant we keep it outside the differential. In (1) the derivative of a sum of the two derivatives as in (2). The second derivative in the bracket of (2) is easy to differentiate in (3) as the variable is L_Y and the differentiation is by L_Y. Substituting (3) into (2) gives us (4).

For the first term in the brackets of (4) the variable is L_X and the differentiation is by L_Y hence we need to use the chain rule of differentiation the separation of variables allows us to cancel out the dz terms in red.

$$\frac{\mathrm{d}\,y}{\mathrm{d}\,x} = \frac{\mathrm{d}\,y}{\mathrm{d}\,z} \times \frac{\mathrm{d}\,z}{\mathrm{d}\,x} \quad \text{Chain rule of differentiation}$$

$$(5) \quad \frac{\mathrm{d}\,E}{\mathrm{d}\,L_Y} = \frac{h^2}{8\,m}\left(\frac{\mathrm{d}}{\mathrm{d}\,L_X}\left(\frac{n_X^2}{L_X^2}\right)\frac{\mathrm{d}\,L_X}{\mathrm{d}\,L_Y} - \frac{2n_Y^2}{L_Y^3}\right)$$

$$(6) \quad \frac{\mathrm{d}\,E}{\mathrm{d}\,L_Y} = \frac{h^2}{8m}\left(-\frac{2\,n_X^2}{L_X^3}\,\frac{\mathrm{d}\,L_X}{\mathrm{d}\,L_Y} - \frac{2\,n_2^2}{L_2^3}\right)$$

$$(7) \quad 0 = \frac{h^2}{8\,m}\left(-\frac{2\,n_X^2}{L_X^3}\,\frac{\mathrm{d}\,L_X}{\mathrm{d}\,L_Y} - \frac{2\,n_Y^2}{L_Y^3}\right)$$

$$(8) \quad \frac{\mathrm{d}\,L_X}{\mathrm{d}\,L_Y} = -\,\frac{n_Y^2}{L_Y^3}\,\frac{L_X^3}{n_X^2}$$

Applying the chain rule to the first term in brackets of (4) gives us (5). The derivative of the first term in the brackets of (5) gives (6). (7) Remembering from the question that the energy E is constant, then dE/dL_Y = 0. In (7) the constant term $h/8m$ cannot be equal to zero, so the term in the brackets must be zero. The derivative asked for is (8).

Rearranging (8) to the equation below gives us a clearer idea what effect altering the lengths of the sides of our quantum well whilst maintaining a constant energy for the particle. The ratios of the length cubed over the quantum number squared for each side are the crucial factors.

$$\frac{\mathrm{d}\,L_X}{\mathrm{d}\,L_Y} = -\,\frac{L_X^3/n_X^2}{L_Y^3/n_Y^2} \quad \text{Altering the size of a quantum well at constant energy}$$

Return to Question 1 (see page 16)

1.3.2 SOLUTION 2: ELECTRONS IN ATOMIC ORBITALS

$$(1) \quad \overbrace{P = \frac{4}{a_0^3}\,r^2\,\mathrm{e}^{-2r/a_0}}^{\textbf{H-atom 1s radial distribution function}}$$

$$(2) \quad \frac{\mathrm{d}\,P}{\mathrm{d}\,r} = \frac{4}{a_0^3}\left(r^2\frac{\mathrm{d}}{\mathrm{d}\,r}\mathrm{e}^{-2\,r/a_0} + \mathrm{e}^{-2\,r/a_0}\,\frac{\mathrm{d}\,r^2}{\mathrm{d}\,r}\right)$$

$$(3) \quad \frac{\mathrm{d}\,P}{\mathrm{d}\,r} = \frac{4}{a_0^3}\left(-\,\frac{2\,r^2}{a_0}\mathrm{e}^{-2\,r/a_0} + 2\,r\,\mathrm{e}^{-2\,r/a_0}\right)$$

The radial distribution function in equation (1) for a 1s H-atom has the constant term $4/a_0{}^3$. In (2) this term is taken outside the brackets. The product rule of differentiation is applied to r^2 and $\exp(-2r/a_0)$ in (3).

$$(4)\quad \frac{\mathrm{d}P}{\mathrm{d}r} = \overbrace{\frac{8r}{a_0^3}}^{\substack{r=0\\ P=0}}\ \overbrace{\mathrm{e}^{-2r/a_0}}^{\substack{r=\infty\\ P=0}} \overbrace{\left(1-\frac{r}{a_0}\right)}^{\substack{r=a_0\\ P=\max}} = 0$$

From (3) we take the common factors outside the brackets and tidy up the equation to give (4). The maximum in the radial distribution function is where the derivative $\mathrm{d}P/\mathrm{d}r$ in (4) is zero. The derivative is equal to zero if *any* of the three terms in (4) are equal to zero. The first term of the derivative is zero at the nucleus $(8r/a_0{}^3) = 0$ at $r = 0$ but the radial distribution function P is also zero at the nucleus. The second term, the negative exponential $\exp(-2r/a_0)$ from Fig. 1.8 equals zero at the asymptote $r = \infty$ where $P = 0$. The third term is zero at the Bohr radius $(1 - r/a_0) = 0$ and $r = a_0$ where the radial distribution function is a maximum at $P = 1.023$.

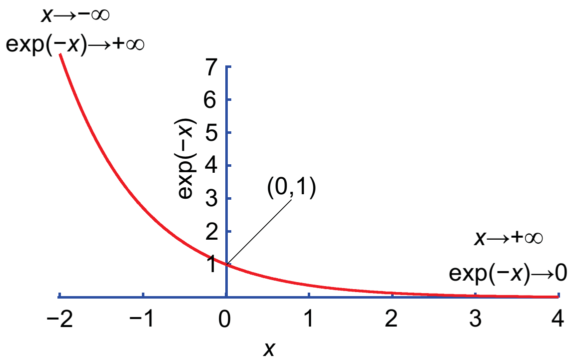

Figure 1.8: a negative exponential function.

$$a_0 = 0.5292 \times 10^{-10} \text{ m}$$ The Bohr radius

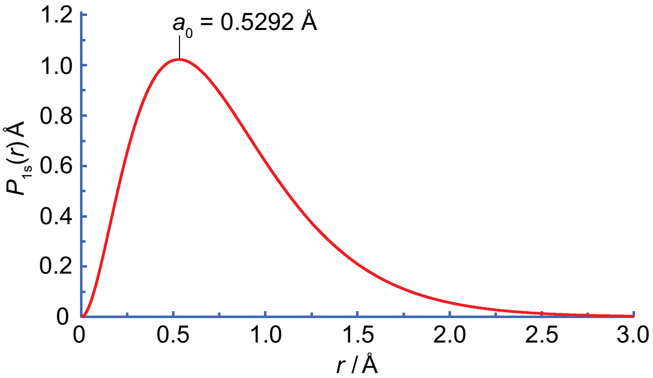

Figure 1.9: H-atom 1s radial distribution function.

Fig 1.9 is the radial distribution function for the 1s H-atom with a_0 = 0.5292 Å the maximum of the radial distribution function has a value of $P_{max}(H_{1s})$ = 1.023 Å^{-1}. The 1s radial distribution depends upon the radius r but not upon the values of x, y, or z. Notice that the radial distribution function extends out to infinity. So how can we visualize the 1s orbital? Fig. 1.10 shows the conventional view of the H-atom 1s atomic orbital (AO) which is a sphere with the centre at the nucleus and the surface is drawn as a contour surface to enclose 90% of the total electron probability. The other atomic and molecular orbitals are also drawn as contour surfaces enclosing 90% of the total electron probability.

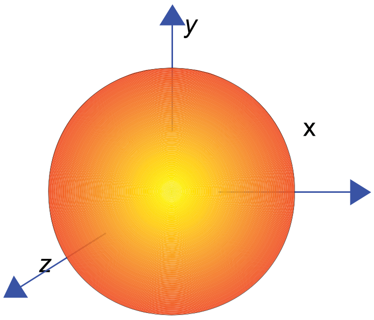

Figure 1.10: H-atom 1s atomic orbital contour surface.

Return to Question 2 (see page 17)

1.3.3 SOLUTION 3: VIBRATION OF MOLECULAR BONDS AND HEAT CAPACITY

$$(1)\quad U^{\mathrm{V}} = nN_{\mathrm{A}}hc\bar{\nu}\,\frac{\mathrm{e}^{-hc\bar{\nu}\beta}}{1-\mathrm{e}^{-hc\bar{\nu}\beta}}$$

(1) Calculating the derivative $\mathrm{d}U^{\mathrm{V}}/\mathrm{d}\beta$ of the heat capacity of our SHO diatomic molecule the term $nN_{\mathrm{A}}hc\bar{\nu}$ is constant so let us concentrate on the ratio of the exponentials.

$$u = \mathrm{e}^{-hc\bar{\nu}\beta} \qquad \frac{\mathrm{d}u}{\mathrm{d}\beta} = -hc\bar{\nu}\,\mathrm{e}^{-hc\bar{\nu}\beta} \qquad v = 1-\mathrm{e}^{-hc\bar{\nu}\beta} \qquad \frac{\mathrm{d}v}{\mathrm{d}\beta} = hc\bar{\nu}\,\mathrm{e}^{-hc\bar{\nu}\beta}$$

$$(2)\quad \frac{\mathrm{d}}{\mathrm{d}\beta}\left(\frac{u}{v}\right) = \frac{\overbrace{\left(1-\mathrm{e}^{-hc\bar{\nu}\beta}\right)}^{v}\overbrace{\left(-hc\bar{\nu}\,\mathrm{e}^{-hc\bar{\nu}\beta}\right)}^{\mathrm{d}u/\mathrm{d}\beta} - \overbrace{\left(\mathrm{e}^{-hc\bar{\nu}\beta}\right)}^{u}\overbrace{\left(hc\bar{\nu}\,\mathrm{e}^{-hc\bar{\nu}\beta}\right)}^{\mathrm{d}v/\mathrm{d}\beta}}{\underbrace{\left(1-\mathrm{e}^{-hc\bar{\nu}\beta}\right)^2}_{v^2}}$$

We use the quotient rule to differentiate the ratio of the exponentials to give (2).

$$(3)\quad \frac{\mathrm{d}(u/v)}{\mathrm{d}\beta} = \frac{-hc\bar{\nu}\,\mathrm{e}^{-hc\bar{\nu}\beta}\overbrace{+hc\bar{\nu}\,\mathrm{e}^{-2hc\bar{\nu}\beta}}^{\text{cancel}}\;\overbrace{-hc\bar{\nu}\,\mathrm{e}^{-2hc\bar{\nu}\beta}}^{\text{cancel}}}{\left(1-\mathrm{e}^{-hc\bar{\nu}\beta}\right)^2}$$

$$(4)\quad \frac{\mathrm{d}(u/v)}{\mathrm{d}\beta} = -hc\bar{\nu}\,\frac{\mathrm{e}^{-hc\bar{\nu}\beta}}{\left(1-\mathrm{e}^{-hc\bar{\nu}\beta}\right)^2}$$

$$(5)\quad \frac{\mathrm{d}U^{\mathrm{V}}}{\mathrm{d}\beta} = -nN_{\mathrm{A}}h^2c^2\bar{\nu}^2\,\frac{\mathrm{e}^{-hc\bar{\nu}\beta}}{\left(1-\mathrm{e}^{-hc\bar{\nu}\beta}\right)^2}$$

The quotient rule of the exponential terms in (2) is multiplied out to give (3) whilst remembering that $(\exp{-x})(\exp{-x}) = \exp(-2x)$. In (3) two of the terms cancel out leading to (4). The differential (4) is multiplied by the constants $nN_{\mathrm{A}}hc\bar{\nu}$ to give $\mathrm{d}U^{\mathrm{V}}/\mathrm{d}\beta$ (5).

$$(6)\quad C_V^{\mathrm{V}} = -k_{\mathrm{B}}\beta^2\,\frac{\mathrm{d}U^{\mathrm{V}}}{\mathrm{d}\beta} \qquad (7)\quad C_V^{\mathrm{V}} = +nN_{\mathrm{A}}h^2c^2\bar{\nu}^2k_{\mathrm{B}}\beta^2\,\frac{\mathrm{e}^{-hc\bar{\nu}\beta}}{\left(1-\mathrm{e}^{-hc\bar{\nu}\beta}\right)^2}$$

From the definition of the vibrational heat capacity in (6) we can multiply (5) by $-k_{\mathrm{B}}\beta^2$ gives the contribution to the heat capacity at constant volume due to harmonic vibrations (7). Equation (7) is very untidy which we tidy up by substituting R for $k_{\mathrm{B}}N_{\mathrm{A}}$ and $1/k_{\mathrm{B}}T$ for the thermodynamic beta.

$$C_V^{\mathrm{V}} = nR\left(\frac{hc\bar{\nu}}{k_{\mathrm{B}}T}\right)^2\frac{\mathrm{e}^{-hc\bar{\nu}/k_{\mathrm{B}}T}}{\left(1-\mathrm{e}^{-hc\bar{\nu}/k_{\mathrm{B}}T}\right)^2} \qquad \text{SHO contribution to heat capacity}$$

Return to Question 3 (see page 18)

2 WEEK 2: CHEMISTRY AND DIFFERENTIATION 2

2.1 WEEK 2 TUTORIAL QUESTIONS

2.1.1 QUESTION 1: CONSECUTIVE CHEMICAL REACTIONS

Chemical reactions may consist of several separate chemical steps. For example, the decay of a radioactive element may result in a daughter isotope which then itself decays. Consecutive chemical reactions are very common in organic, inorganic and biochemical reactions. An organic chemistry example is the reaction of *tert*-butyl bromide (2-bromo-2-methyl-propane) dissolved in water containing a small concentration of sodium hydroxide. In chemistry this reaction is an example of an S_N1 reaction. The first reaction is slow and is the loss of bromide ion Br^- from the *tert*-butyl bromide to form a *tert*-butyl carbocation, Figs 2.1.

$$(CH_3)_3C{-}Br \xrightarrow{\curvearrowright\ \text{slow}} (CH_3)_3C^+ + Br^-$$

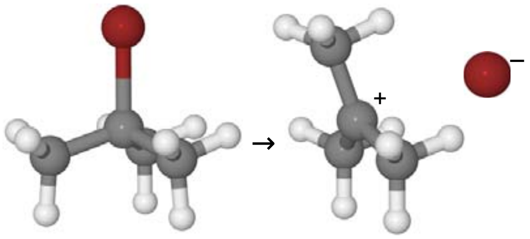

Figure 2.1: S_N1 the first slow reaction, dark grey C, grey H, dark red Br.

A second reaction is fast and is the covalent bond formation between a solvated hydroxide ion and a solvated *tert*-butyl carbocation to form the product molecule, a tertiary alcohol, *tert*-butanol. For clarity the solvent in not shown.

$$(CH_3)_3C^+ \ \overset{\curvearrowleft}{}\ {}^-OH \xrightarrow{\text{fast}} (CH_3)_3C{-}OH$$

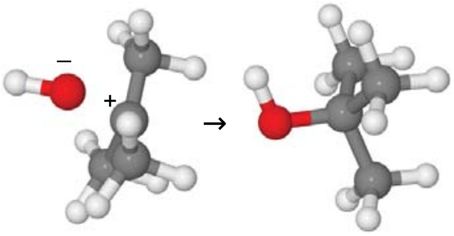

Figure 2.2: S_N1 fast second reaction, dark grey C, grey H, red O.

For simplicity let us consider the simplest possible consecutive reactions consisting of two non-reversible steps where both of the steps are first-order. In the first reaction the reactant A forms the reaction intermediate I with a rate constant k_a. In the second reaction the reaction intermediate I forms the reaction product P with a rate constant k_b.

$$\underset{\text{reactant}}{A} \xrightarrow{k_a} \underset{\text{intermediate}}{I} \xrightarrow{k_b} \underset{\text{product}}{P}$$

At any given time t the concentrations of A, I, and P can be expressed as (1), (2), and (3) in terms of the initial concentration $[A]_0$ if there is no intermediate or product initially present at zero time.

$$(1)\quad [A] = [A]_0 e^{-k_a t}$$

$$(2)\quad [I] = [A]_0 \frac{k_a}{k_b - k_a}\left(e^{-k_a t} - e^{-k_b t}\right)$$

$$(3)\quad [P] = [A]_0 \left(1 - \frac{k_b}{k_b - k_a} e^{-k_a t} + \frac{k_a}{k_b - k_a} e^{-k_b t}\right)$$

First, determine d[P]/d[I] using the ‘parametric derivative’ method which arises by manipulation of the chain rule of differentiation. Secondly, approximate this general expression for d[P]/d[I] for when the rate constants are $k_a \ll k_b$ that is a slow first reaction followed by a fast second reaction.

Jump to Solution 1 (see page 29)

2.1.2 QUESTION 2: VIBRATIONAL ENERGY OF A COLLECTION OF MOLECULES

From quantum mechanics we know that all molecules are vibrating all the time, even at zero kelvin their bonds are never stationary. This is a consequence of the Heisenberg uncertainty principle (Parker 2015, Section 3). The bond distance of a vibrating diatomic molecule oscillates between a minimum value and a maximum value. Similarly a vibrational mode may also be the bond angle increasing and decreasing between three atoms in a molecule. The resistance of the bond to stretching or a bond angle to bending is called the force constant k and the displacement from equilibrium position is $(r - r_e)$ or $(\theta - \theta_e)$. As a first approximation the vibrations may be treated rather like a mechanical spring (Hooke’s law) and the potential energy V due to the vibration of bond stretching or bond angle bending are parabolic in shape, the equations for the potential energy V are below and the potential energy is the red parabola in Fig. 2.3. Treating the potential energy of a vibrating bond like a mechanical spring as in Hooke’s law is called the ‘simple harmonic oscillator’ (SHO) approximation, it is a first-approximation which is valid near the bottom of the potential well.

$$V_{\text{stretch}} = \frac{1}{2}k_{\text{stretch}}(r - r_e)^2 \qquad V_{\text{bend}} = \frac{1}{2}k_{\text{bend}}(\theta - \theta_e)^2 \quad \text{SHO potential energy}$$

Where k is the force constant or the ‘stiffness’ of the bond. The total vibrational energy E_v of a diatomic molecule is the sum of the kinetic and potential energies and does not vary with bond distance or bond angle (blue horizontal lines in Fig. 2.3) and is quantized.

$$E_v = (v + ½)h\nu \quad \text{Simple harmonic oscillator}$$

The vibrational quantum number v (vee) and v = 0, 1, 2,… and the frequency ν (nu) is shown below where μ (mu) is the effective mass of the vibrational mode.

$$\nu = \frac{1}{2}\sqrt{\frac{k}{\mu}} \quad \text{Vibration frequency, } \mu \text{ is the effective mass}$$

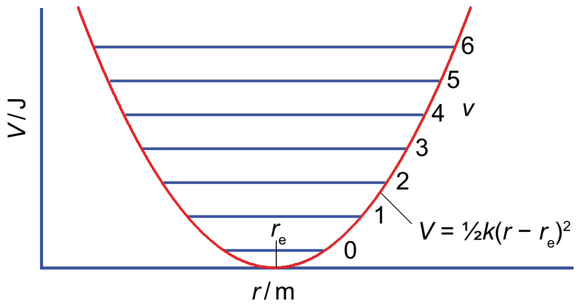

Figure 2.3: diatomic harmonic oscillator.

At thermal equilibrium the total vibrational energy E^V for n moles of a diatomic molecule treated as harmonic oscillators is shown below.

$$E^{\mathrm{V}} = n N_{\mathrm{A}} h c \bar{\nu} \frac{\mathrm{e}^{-hc\bar{\nu}\beta}}{1-\mathrm{e}^{-hc\bar{\nu}\beta}}$$ Total vibrational energy of n moles of diatomic molecules

Where: the thermodynamic beta β is equal to $1/k_{\mathrm{B}}T$ with k_{B} is Boltzmann's constant, T is the absolute temperature, $\bar{\nu}$ (nu bar) is the vibrational wavenumber not to be confused with the vibrational quantum number 'v' (vee), N_{A} is Avogadro's constant, h is Planck's constant, and c is the velocity of light.

Use the Maclaurin series expansion of $\exp(-hc\bar{\nu}\beta)$ to approximate the expression for E^V at high temperatures, that is when $hc\bar{\nu}\beta \ll 1$.

Jump to Solution 2 (see page 32)

2.1.3 QUESTION 3: CHEMICAL REACTION WITH FIRST-ORDER KINETICS

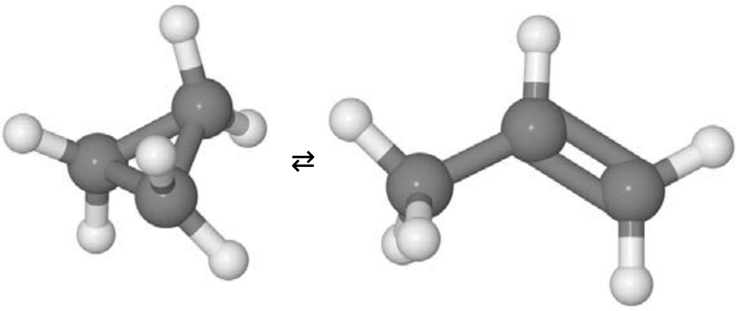

Figure 2.4: cyclopropane to propene isomerization, grey C, and light grey H.

An example of a first-order reaction is the isomerization from cyclopropane to propene which occurs at around 500 °C. The double full-arrows indicate that the reaction can occur starting from either the 'reactants' or 'products' and may not yet have reached equilibrium. The integrated rate law for a first-order reaction is as follows.

$$k\,t = \ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x}$$ Integrated first-order rate law

Where k is the rate constant, $[\mathrm{A}]_0$ the original concentration of reactant (cyclopropane in the example), and x is the concentration of A that has been lost through reaction at a time t. Expand $\ln([\mathrm{A}]_0 - x)$ using a Taylor series, and show that when $[\mathrm{A}]_0$ » x, early in the reaction, the rate of reaction is approximately linear in x.

Jump to Solution 3 (see page 33)

2.2 WEEK 2 TUTORIAL SOLUTIONS

2.2.1 SOLUTION 1: CONSECUTIVE CHEMICAL REACTIONS

The solution to this question is a little long in time but each step is not complicated, you have to keep your nerve and not get lost because of the length of the solution. We have to calculate d[P]/d[I] from the concentrations of the intermediate molecule [I] and the product molecule [P]. This is an example of the 'parametric derivative' method where the time *t* is a parameter of both [I] and [P]. The chain rule may be rearranged to give the required parametric derivative.

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = \overbrace{\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}[\mathrm{I}]} \times \frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}}^{\textbf{chain rule}}$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}[\mathrm{I}]} = \frac{\dfrac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}}{\dfrac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}} \quad \text{Example of a parametric derivative}$$

$$(1) \quad [\mathrm{P}] = [\mathrm{A}]_0\left(1 - \frac{k_\mathrm{b}}{k_\mathrm{b}-k_\mathrm{a}}\mathrm{e}^{-k_\mathrm{a}t} + \frac{k_\mathrm{a}}{k_\mathrm{b}-k_\mathrm{a}}\mathrm{e}^{-k_\mathrm{b}t}\right)$$

$$(2) \quad \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = [\mathrm{A}]_0\left(\frac{k_\mathrm{a}k_\mathrm{b}}{k_\mathrm{b}-k_\mathrm{a}}\mathrm{e}^{-k_\mathrm{a}t} - \frac{k_\mathrm{a}k_\mathrm{b}}{k_\mathrm{b}-k_\mathrm{a}}\mathrm{e}^{-k_\mathrm{b}t}\right)$$

$$(3) \quad \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = [\mathrm{A}]_0\frac{k_\mathrm{a}k_\mathrm{b}}{k_\mathrm{b}-k_\mathrm{a}}\left(\mathrm{e}^{-k_\mathrm{a}t} - \mathrm{e}^{-k_\mathrm{b}t}\right)$$

The product concentration [P] in (1) is differentiated in (2) and tidied up in (3).

$$(4) \quad [\mathrm{I}] = [\mathrm{A}]_0\frac{k_\mathrm{a}}{k_\mathrm{b}-k_\mathrm{a}}\left(\mathrm{e}^{-k_\mathrm{a}t} - \mathrm{e}^{-k_\mathrm{b}t}\right)$$

$$(5) \quad \frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = [\mathrm{A}]_0\frac{k_\mathrm{a}}{k_\mathrm{b}-k_\mathrm{a}}\left(-k_\mathrm{a}\mathrm{e}^{-k_\mathrm{a}t} + k_\mathrm{b}\mathrm{e}^{-k_\mathrm{b}t}\right)$$

The intermediate concentration [I] in (4) is differentiated in (5). The two derivatives d[P]/d*t* (3) and d[I]/d*t* (5) are used in the parametric derivative expression (6) which is tidied up to (7).

$$(6) \quad \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}[\mathrm{I}]} = \frac{\dfrac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}}{\dfrac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}} = \frac{[\mathrm{A}]_0\dfrac{k_\mathrm{a}k_\mathrm{b}}{k_\mathrm{b}-k_\mathrm{a}}\left(\mathrm{e}^{-k_\mathrm{a}t} - \mathrm{e}^{-k_\mathrm{b}t}\right)}{[\mathrm{A}]_0\dfrac{k_\mathrm{a}}{k_\mathrm{b}-k_\mathrm{a}}\left(-k_\mathrm{a}\mathrm{e}^{-k_\mathrm{a}t} + k_\mathrm{b}\mathrm{e}^{-k_\mathrm{b}t}\right)}$$

$$(7) \quad \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}[\mathrm{I}]} = k_\mathrm{b}\frac{\left(\mathrm{e}^{-k_\mathrm{a}t} - \mathrm{e}^{-k_\mathrm{b}t}\right)}{\left(-k_\mathrm{a}\mathrm{e}^{-k_\mathrm{a}t} + k_\mathrm{b}\mathrm{e}^{-k_\mathrm{b}t}\right)}$$

The general solution (7) is true for *all* values of the two first-order rate constants. We want to find the approximate solution for a slow first reaction followed by a fast second reaction, $k_a \ll k_b$.

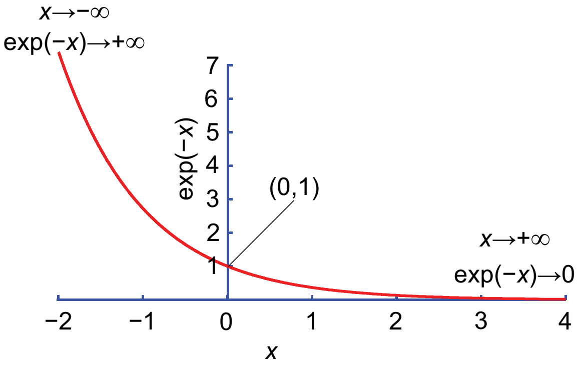

Figure 2.5: negative exponential function.

From the graph of a negative exponential Fig. 2.5, for the rate constants $k_a \ll k_b$ with both positive quantities, the exponentials $\exp(-k_a t) \approx 1$ and $\exp(-k_b t) \approx 0$ allows us to approximate the general solution (7) to the specific situation (9).

$$(8) \quad \frac{d[P]}{d[I]} = k_b \frac{\left(e^{-k_a t} - e^{-k_b t}\right)}{\left(-k_a e^{-k_a t} + k_b e^{-k_b t}\right)} \approx k_b \frac{(1-0)}{(-k_a \times 1 + k_b \times 0)}$$

$$(9) \quad \frac{d[P]}{d[I]} \approx -\frac{k_b}{k_a}$$

The derivative d[P]/d[I] is not the ratio of two concentrations. It is the change in the product concentration due to a change in the intermediate concentration and is a large negative number.

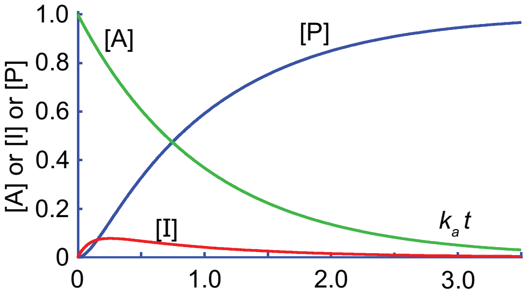

Figure 2.6: concentrations versus time for k_a/k_b = 1/10.

Our approximations of the two functions for $\exp(-kt)$ are valid when the time t is not close to zero and it is past the 'induction period' when [I] goes through a maximum, and when the time is not exceedingly large when both functions for $\exp(-kt)$ approach zero. Fig. 2.6 is plotted as an example with $k_a/k_b = 1/10$ with first step being 10 times slower than the second step. Fig. 2.6 shows that after [I] has passed through its maximum its value decreases (a negative gradient) and [P] increases with a positive gradient which is 10 times larger for our example. This situation corresponds to what is called 'steady state approximation' of the intermediate (see Parker 2018, section 6.2.8).

$$(3)\quad \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = [\mathrm{A}]_0 \frac{k_{\mathrm{a}} k_{\mathrm{b}}}{k_{\mathrm{b}} - k_{\mathrm{a}}}\left(\mathrm{e}^{-k_{\mathrm{a}} t} - \mathrm{e}^{-k_{\mathrm{b}} t}\right)$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} \approx k_a [\mathrm{A}]_0$$ S_N1 (substitution nucleophilic unimolecular) rate law

From equation (3) of the derivative of the product concentration with time we use the same approximations as previously $\exp(-k_a t) \approx 1$, $\exp(-k_b t) \approx 0$, and $(k_b - k_a) \approx k_b$ which gives an approximate rate law which is first-order in the reactant concentration with a rate constant of k_a the first slow reaction. Hence the symbol S_N1 for 'unimolecular nucleophilic substitution'.

Return to Question 1 (see page 24)

2.2.2 SOLUTION 2: VIBRATIONAL ENERGY OF A COLLECTION OF MOLECULES

We are going to use a Maclaurin series expansion of $f(x) = \exp(-hc\bar{\upsilon}\beta)$ and then approximate the series for when the temperature is high (β is small) and $hc\bar{\upsilon}\beta \ll 1$.

$$(1)\quad \frac{\mathrm{d}}{\mathrm{d}\beta}\left(\mathrm{e}^{-hc\bar{\upsilon}\beta}\right) = -hc\bar{\upsilon}\,\mathrm{e}^{-hc\bar{\upsilon}\beta} \qquad (2)\quad \frac{\mathrm{d}}{\mathrm{d}\beta}(\beta=0) = -hc\bar{\upsilon}$$

$$(3)\quad \frac{\mathrm{d}}{\mathrm{d}\beta^2}\left(\mathrm{e}^{-hc\bar{\upsilon}\beta}\right) = h^2c^2\bar{\upsilon}^2\,\mathrm{e}^{-hc\bar{\upsilon}\beta} \qquad (4)\quad \frac{\mathrm{d}}{\mathrm{d}\beta^2}(\beta=0) = h^2c^2\bar{\upsilon}^2$$

$$(5)\quad \frac{\mathrm{d}}{\mathrm{d}\beta^3}\left(\mathrm{e}^{-hc\bar{\upsilon}\beta}\right) = -h^3c^3\bar{\upsilon}^3\,\mathrm{e}^{-hc\bar{\upsilon}\beta} \qquad (6)\quad \frac{\mathrm{d}}{\mathrm{d}\beta^3}(\beta=0) = -h^3c^3\bar{\upsilon}^3$$

The first, second, and third derivatives of the exponential are taken in (1), (3), and (5). Each of these derivatives is then evaluated when β is zero in (2), (4), and (6). Note the alternation of signs for even and odd powers in (2), (4), and (6).

$$(7)\quad f(x) = f(0) + x\frac{\mathrm{d}}{\mathrm{d}x}f(0) + \frac{x^2}{2!}\frac{\mathrm{d}^2}{\mathrm{d}x^2}f(0) + \frac{x^3}{3!}\frac{\mathrm{d}^3}{\mathrm{d}x^3}f(0) + \ldots$$

$$(8)\quad \mathrm{e}^{-hc\bar{\upsilon}\beta} = 1 - \beta hc\bar{\upsilon} + \frac{\beta^2}{2}h^2c^2\bar{\upsilon}^2 - \frac{\beta^3}{6}h^3c^3\bar{\upsilon}^3 + \ldots$$

$$(9)\quad \mathrm{e}^{-hc\bar{\upsilon}\beta} \approx 1 - hc\bar{\upsilon}\beta$$

The Maclaurin series (7) is in our example $f(x) = \exp(-hcv\beta)$ and $x = \beta$. Substitution of the derivatives (2), (4), and (6) and x gives (8). As the temperature is high (β is small) in (8) we can drop the squared and higher powered terms of β in the series to get the approximation for high temperatures in (9) $\exp(-hcv\beta) \approx (1-hcv\beta)$.

$$(10)\quad E^{\mathrm{V}} = nN_{\mathrm{A}}hc\bar{\upsilon}\frac{\mathrm{e}^{-hc\bar{\upsilon}\beta}}{1-\mathrm{e}^{-hc\bar{\upsilon}\beta}} \qquad (11)\quad E^{\mathrm{V}} \approx nN_{\mathrm{A}}hc\bar{\upsilon}\frac{1-hc\bar{\upsilon}\beta}{1-(1-hc\bar{\upsilon}\beta)}$$

$$(12)\quad E^{\mathrm{V}} \approx nN_{\mathrm{A}}hc\bar{\upsilon}\frac{1-hc\bar{\upsilon}\beta}{hc\bar{\upsilon}\beta} \qquad (13)\quad E^{\mathrm{V}} \approx \frac{nN_{\mathrm{A}}}{\beta}(1-hc\bar{\upsilon}\beta)$$

$$(14)\quad E^{\mathrm{V}} \approx \frac{nN_{\mathrm{A}}}{\beta} \qquad (15)\quad E^{\mathrm{V}} \approx nN_{\mathrm{A}}k_{\mathrm{B}}T$$

Substituting the approximation (9) into (10) gives (11), the expression for the vibrational energy of n moles of diatomic simple harmonic oscillators. The approximate vibrational energy (11) cleans up to (12) and then (13). We use $hcv\beta \ll 1$ to approximate the term in brackets in (13) to obtain (14). In (14) we substitute for the thermodynamic beta with $1/k_{\mathrm{B}}T$ to give (15). The product of Avogadro's constant and Boltzmann's constant is replaced by the gas constant R to give the high temperature limit of the vibrational energy of n moles of diatomic simple harmonic oscillators.

$E^{\mathrm{V}} \approx nRT$ Vibrational energy of n moles of SHO diatomics in the high temperature limit

This is an example of the equipartition theorem which is a classical result valid when quantum effects may be ignored. The approximation is an example of the 'correspondence principle' (Parker 2015, sections 171 and 3.1), there is no sharp boundary between classical and quantum mechanics for high energies (high temperatures in this case).

The correspondence principle: the quantum mechanics results for a system which has large containment sizes compared with molecular sizes, or for large quantum numbers (large quantum energies) leads smoothly and continuously to the non-quantized classical Newtonian mechanics solution.

Return to Question 2 (see page 26)

2.2.3 SOLUTION 3: CHEMICAL REACTION WITH FIRST ORDER KINETICS

$$(1)\quad kt = \ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x} \qquad (2)\quad kt = \ln[\mathrm{A}]_0 - \ln([\mathrm{A}]_0 - x)$$

For a reaction with first-order kinetics we need to find the rate of reaction at short times when $[\mathrm{A}]_0$ » x. The integrated first-order kinetics rate law (1) for the isomerization of cyclopropane to propene reaction has the log rearranged to equation (2).

$$(3)\quad f(a-x) = f(a) - x\frac{\mathrm{d}f(a)}{\mathrm{d}x} + \frac{x^2}{2!}\frac{\mathrm{d}^2 f(a)}{\mathrm{d}x^2} - \frac{x^3}{3!}\frac{\mathrm{d}^3 f(a)}{\mathrm{d}x^3} + \ldots$$

$$(4)\quad f(\ln[\mathrm{A}]_0 - x) = \ln[\mathrm{A}]_0 - x\left(\frac{1}{[\mathrm{A}]_0}\right) + \frac{x^2}{2!}\left(\frac{-1}{[\mathrm{A}]_0^2}\right) - \frac{x^3}{3!}\left(\frac{2}{[\mathrm{A}]_0^3}\right) + \ldots$$

$$(5)\quad f(\ln[\mathrm{A}]_0 - x) = \ln[\mathrm{A}]_0 - \frac{x}{[\mathrm{A}]_0} - \frac{x^2}{2[\mathrm{A}]_0^2} - \frac{x^3}{3[\mathrm{A}]_0^3} + \ldots$$

We now use the Taylor series (3) to expand the $\ln([\mathrm{A}]_0 - x)$ term in (4) and taking the minus signs outside the brackets gives (5).

$$(6)\quad kt = \overbrace{\ln[\mathrm{A}]_0}^{\text{cancel}} - \left(\overbrace{\ln[\mathrm{A}]_0}^{\text{cancel}} - \frac{x}{[\mathrm{A}]_0} - \frac{x^2}{2[\mathrm{A}]_0^2} - \frac{x^3}{3[\mathrm{A}]_0^3} + \ldots\right)$$

$$(7)\quad kt = \frac{x}{[\mathrm{A}]_0} + \frac{x^2}{2[\mathrm{A}]_0^2} + \frac{x^3}{3[\mathrm{A}]_0^3} + \ldots$$

$$(8)\quad kt \approx \frac{x}{[\mathrm{A}]_0}$$

$$(9)\quad v_0 = k[\mathrm{A}]_0 \approx \frac{x}{t}$$

Substitute the Taylor series expansion (5) for $\ln([A]_0 - x)$ into the integrated rate law (2) gives (6). The $\ln[A_0]$ terms cancel gives the series (7). At short reaction times the original concentration of the cyclopropane is much larger than the concentration of the product propene, that is $[A]_0 \gg x$ and we may approximate the series by ignoring the square and higher powers of x to give equation (8). The initial rate of reaction (9) at very small times for a first-order reaction is approximately linear in x/t. As both x (the concentration of propene in our example) and t are small quantities their ratio may be subject to large errors unless precise data is available to measure the initial rate.

Fig. 2.7 plots in red the $x/[A]_0$ for the cyclopropane to propene isomerization which at 500 °C has a rate constant of 6.71×10^{-4} s^{-1} and a half-life of 17.2 s. The green line is the initial rate (the tangent to the curve at zero time). Note that the initial rate deviates from the experiential results from ~50 seconds. To obtain rapidly a large number of precise and very small experimental concentrations is a problem which needs careful design of the apparatus and the method used for fast, accurate, repetitive chemical analysis.

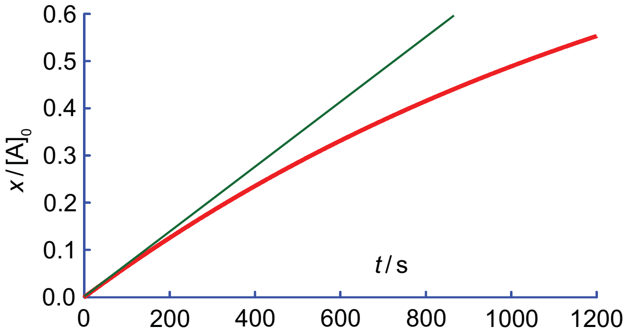

Figure 2.7: cyclopropane to propene isomerization at 500 °C in the gas phase.

Return to Question 3 (see page 27)

3 WEEK 3: CHEMISTRY AND FIRST-ORDER ORDINARY DIFFERENTIAL EQUATIONS

3.1 INTRODUCTION TO ORDINARY DIFFERENTIAL EQUATIONS

An ordinary differential equation (ODE) is an equation between a dependent variable y and one independent variable x and one or more derivatives of y with respect to x. Three example of ordinary differential equations are (1), (2), and (3) where a, b, c, and d are constants.

$$(1)\quad a\frac{\mathrm{d}y}{\mathrm{d}x} + by + c = 0$$

$$(2)\quad a\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + b\frac{\mathrm{d}y}{\mathrm{d}x} + cy + d = 0$$

$$(3)\quad a\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + by + c = 0$$

Ordinary differential equations represent dynamic situations, that is where quantities are changing and such situations are very common in chemistry, physics, biology and chemical engineering. A simple example of an ordinary differential equation is Newton's second law of motion that the force at a certain time F equals mass times the acceleration.

$$F = m\frac{d^2x}{dt^2}$$ An ordinary differential equation, Newton's second law of motion

The word 'ordinary' is to distinguish between where y is a function of one variable x from partial differential equations where the y is a function of several variables x, z,…

3.1.1 FIRST-ORDER ORDINARY DIFFERENTIAL EQUATIONS

$$a\frac{dy}{dx} + by + c = 0$$ First-order ordinary differential equation

This type of ordinary differential equations is called a first-order differential equation as it involves the first derivative as the highest derivative. The use of the term order in maths to describe an ODE must not be confused with the use of the term order in chemistry to describe the kinetic behaviour of reactions. Thus a second-order rate of reaction might involve an equation similar to either (1) or (2) below, both of which are first-order ordinary differential equations.

$$(1)\quad \frac{d[A]}{dt} = k[A]^2 \qquad (2)\quad \frac{d[A]}{dt} = k[A][B]$$

First-order ODEs are common in chemical kinetics where we are measuring the speed or rate of an event, eg the rate of chemical reaction or the rate of diffusion. If the first-order ordinary differential equation (3) can be rearranged to be in the form (4) it can be solved by direct integration (see Parker 2018, sections 7 and 8). One the other hand, if the first-order ODE is of the form (5) it can be solved by the separation of the variables method (see Parker 2018, section 7.2.1).

$$(3)\quad \frac{dy}{dx} = f(x) \qquad (4)\quad \int dy = \int f(x)dx \qquad (5)\quad \frac{dy}{dx} = f(x,y)$$

Either of these methods of solution will lead to a constant of integration which may be found knowing one boundary condition, for example, in kinetics it might be the initial concentration of the reactant $[A]_0$ at time equal to zero, $t = 0$. The maths of first-order differential equations are also used to locate the turning points (maxima, minima, and points of inflexion) of plots of physical data. First-order ordinary differential equations tutorial questions will be covered in Week 3.

3.1.2 SECOND-ORDER ORDINARY DIFFERENTIAL EQUATIONS

The other type of ODE that commonly occurs is the second-order ODE. A second-order ordinary differential equation involved the second derivative as the highest derivative where *a*, *b*, *c*, *d* are constants. Second-order ODE will be covered in Week 4.

$$a\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + b\frac{\mathrm{d}y}{\mathrm{d}x} + cy + d = 0$$ Second-order ordinary differential equation

3.2 WEEK 3 TUTORIAL QUESTIONS

3.2.1 QUESTION 1: RECOMBINATION OF IODINE ATOMS IN THE GAS PHASE

Iodine atoms in the gas phase recombine with one another to form an iodine molecule.

$$2\,\mathrm{I}^{\bullet} \rightarrow \mathrm{I}_2$$

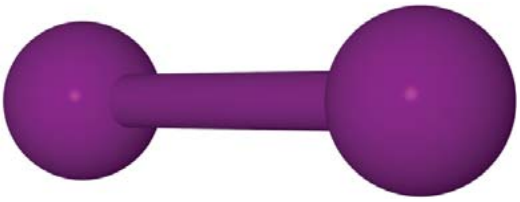

Figure 3.1: iodine molecule.

The reaction has a second-order kinetic rate law for loss of iodine atoms which is a first-order ordinary differential equation.

$$-\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = k[\mathrm{I}]^2$$

The fact that the rate law involves the square of the iodine atom concentration and the stoichiometric equation also involves two iodine atoms is pure coincidence and is not an indication of the reaction mechanism.

$$\mathrm{I}^{\bullet} + \mathrm{I}^{\bullet} \rightarrow \mathrm{I}_2^{*\mathrm{V}} \qquad \mathrm{I}_2^{*\mathrm{V}} + \mathrm{M} \rightarrow \mathrm{I}_2 + \mathrm{M}^{*\mathrm{V}\text{ or }*\mathrm{T}}$$

The atom recombination forms a nascent $\mathrm{I}_2^{*\mathrm{V}}$ where *V means vibrationally excited molecule which contains the bond dissociation energy present as vibrational excitation energy and would dissociate with ~10^{-13} s or half a vibration period to reform iodine atoms. The vibrationally excited molecule $\mathrm{I}_2^{*\mathrm{V}}$ must lose its vibrational energy by a collision in less than ~10^{-13} s with another atom or molecule called a third-body M. In the collision M becomes either vibrationally and/or translationally excited. As the third-body concentration [M] is constant during the reaction it may be ‘ignored’ as far as the rate law is concerned.

At 23 °C in the gas phase this reaction has a rate constant of $k = 7.0\times10^{9}$ L mol^{-1} s^{-1}. Using the separation of variables method solve the first-order ODE rate law to find [I] the iodine atom concentration after 1.5 s if the boundary condition is $[\mathrm{I}]_0 = 6.72\times10^{-3}$ mol L^{-1} at $t = 0$ s.

Jump to Solution 1 (see page 42)

3.2.2 QUESTION 2: BEER-LAMBERT LAW AND THE ABSORPTION OF LIGHT BY MOLECULES

In the lab or in a chemical plant production line a typical method of measuring the concentration of molecules in a solution is to measure the amount of light absorbed in a beam of light of a known wavelength λ and incident intensity I_0 see Fig. 3.2.

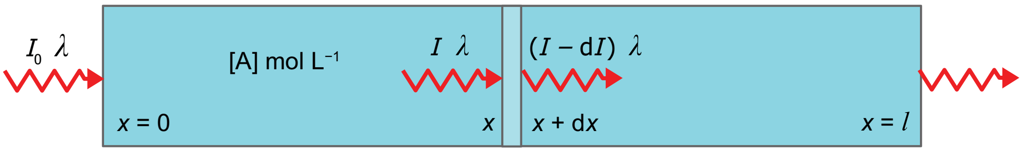

Figure 3.2: quantitative absorption of monochromatic light by molecules in solution.

In the solution the intensity of light decreases by $-\mathrm{d}I$ in a small distance $+\mathrm{d}x$ as it moves away from the source owing to the absorption by previously encountered molecules. The probability of absorption by molecules at a distance x along the decreasing intensity of the beam of light is proportional to the 'local' intensity of the light I and also the number of molecules, that is concentration multiplied by volume $[\mathrm{A}]\times V$. The volume for unit area is just the length $\mathrm{d}x$ so concentration by volume per unit area is $[\mathrm{A}]\times\mathrm{d}x$. Hence the decrease in intensity $-\mathrm{d}I$ of a parallel beam of light, per unit area of the solution, in a distance $\mathrm{d}x$ along the beam's direction due to a concentration of absorber molecules [A] is shown below.

$$-\mathrm{d}I = \kappa I[\mathrm{A}]\mathrm{d}x$$

Where the constant κ (kappa) is the strength of absorption of the light by the molecule at the given wavelength. Rearranging this equation for absorption is a first-order ODE $-\mathrm{d}I/\mathrm{d}x = \kappa I[\mathrm{A}]$.

Solve this first-order ODE for the intensity I for light transmitted through the total length l of solution assuming that the original intensity is I_0 that is the boundary condition is $I = I_0$ at $x = 0$. Convert your solution to a form consistent with $\log_{10}$ rather that natural logs. Convert κ (kappa) to the equivalent $\log_{10}$ absorption coefficient ε (epsilon) with the conventional units of L mol^{-1} cm^{-1}.

Chlorophyll-*a* (Fig. 3.3) is one of the two main photosynthetic pigments present in the leaves of all higher plants. It absorbs strongly in the 400-500 nm range (blue) and less strongly in the 650-700 nm range (red) but lets most of the green-yellow light through and thus leaves appears greenish.

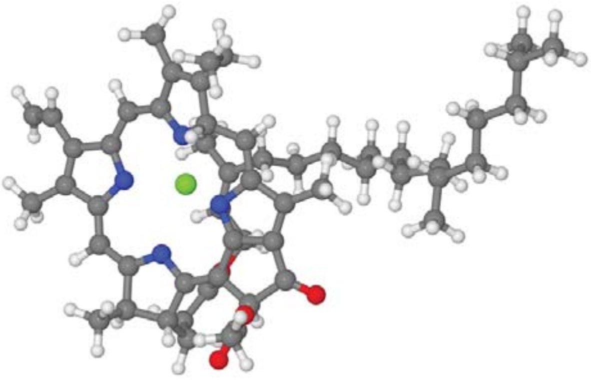

Figure 3.3: chlorophyll-*a* with dark grey C, grey H, red O, blue N, green Mg^{2+}.

A biochemist needs to measure the concentration of chlorophyll-*a*. A solution in methanol is placed in a 1 cm length optical cell and the solution transmits 1.5% of the incident light at a wavelength of 417.8 nm. If the absorption coefficient was previously measured as 1.117×10^5 L mol^{-1} cm^{-1} at 417.8 nm, calculate the concentration of the chlorophyll-*a* solution.

Jump to Solution 2 (see page 43)

3.2.3 QUESTION 3: DIFFUSION OF MOLECULES IN LIQUIDS, GASES OR SOLIDS

Diffusion of molecules in a gas or liquid or solid takes place by the molecules making a series of short steps, each step begins and ends by a collision with another molecule which causes a random change in direction and speed. The molecules movement is called a 'random-walk'. If there is a concentration gradient of the molecule then there will be an overall movement of the molecule from the high concentration towards the low concentration.

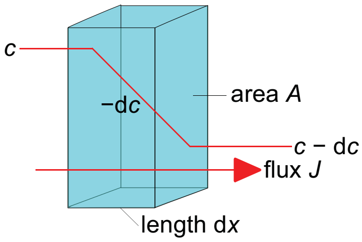

Figure 3.4: linear concentration gradient of a molecule.

In Fig. 3.4 there is a linear concentration falling from left to right by $-\mathrm{d}c$ along a length $+\mathrm{d}x$ and cross-sectional area A of the container. The flux of molecules (the rate of flow of molecules) J mol m^{-2} s^{-1} diffusing per unit area and per unit time is given by Fick's first law of diffusion.

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}x} \quad \text{Fick's first law of diffusion}$$

The negative sign is because a positive flux (flow of molecules) from left to right occurs with a negative concentration gradient. The diffusion constant D m^2 s^{-1} varies from one molecule to another and depends upon the solvent. In order for the units to be consistent the concentration c must be in mol m^{-3} and the distance x in metres.

The average net distance travelled along the concentration gradient by an individual molecule from its starting position in a time t during its random-walk is called the 'root mean square displacement' $\langle \Delta x^2 \rangle^{1/2}$ given by the Einstein-Smoluchowski equation.

$$<\Delta x^2>^{1/2} = \sqrt{2Dt}$$ Einstein-Smoluchowski equation

Diffusion is an important aspect of processes as diverse as the passage of some ions and molecules through biological cell walls, respiration, fluid dynamics of both jet engines and blood in your veins and arteries, drug absorption, semiconductor fabrication, flames, combustion, and explosions, to name but a few!

Sucrose in water at 20 °C and 1 atmosphere pressure has a diffusion constant of $D = 0.522\times10^{-9}$ m^2 s^{-1}. A membrane of 1.5 micron (1.5×10^{-6} m) width and area 2.4×10^{-6} m^2 separates two sucrose solutions with a concentration difference is 0.1 mol L^{-1}. First, calculate how many moles of sucrose pass through the membrane in 10 minutes. Secondly, calculate the average net distance $\sqrt{<\Delta x^2>}$ travelled by an individual sucrose molecule in this time.

Jump to Solution 3 (see page 44)

3.2.4 QUESTION 4: THE AVERAGE SPEED OF GAS MOLECULES

The distribution of speeds c (ignoring the direction of travel) of gas molecules is given by the Maxwell-Boltzmann speed distribution. Where M is the molar mass in kg mol^{-1}, R is the gas constant, and T is the temperature.

$$f(c) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} c^2 e^{-Mc^2/2RT}$$ Maxwell-Boltzmann speed distribution

$$(1)\quad <c> = \int_{c=0}^{c=\infty} c.f(c)\,dc \qquad (2)\quad <c> = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_{c=0}^{c=\infty} c^3 e^{-Mc^2/2RT}\,dc$$

The average molecular speed (1) at a temperature T is $<c>$ and is the integral of the Maxwell-Boltzmann speed distribution multiplied by the speed c between the limits zero and infinity. In (2) the constant terms are taken outside the integral for clarity.

Integrate expression (2) to find the average speed of gas molecules. Secondly, find the average speed of N_2 molecules ($M = 28.02\times10^{-3}$ kg mol^{-1}) at 298.15 K (25°C) given $R = 8.3145$ J K^{-1} mol^{-1}.

Jump to Solution 4 (see page 45)

3.3 WEEK 3 TUTORIALS SOLUTIONS

3.3.1 SOLUTION 1: RECOMBINATION OF IODINE ATOMS IN THE GAS PHASE

$$(1)\quad -\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = k[\mathrm{I}]^2 \qquad (2)\quad \frac{\mathrm{d}[\mathrm{I}]}{[\mathrm{I}]^2} = -k\,\mathrm{d}t \qquad (3)\quad \int_{[\mathrm{I}]_0}^{[\mathrm{I}]} \frac{\mathrm{d}[\mathrm{I}]}{[\mathrm{I}]^2} = -k\int_0^t \mathrm{d}t$$

$$(4)\quad \left[-\frac{1}{[\mathrm{I}]}\right]_{[\mathrm{I}]_0}^{[\mathrm{I}]} = -k\,[t]_0^t + C \qquad (5)\quad -\frac{1}{[\mathrm{I}]} - \left(-\frac{1}{[\mathrm{I}]_0}\right) = -k\,t$$

The rate law (1) is rearranged to (2) by the separation of variables method so that the terms involving iodine atoms concentrations are on the left and on the right hand side is everything else. In the integral equation (3) the constant $(-k)$ is placed outside the integral sign for clarity and the upper and lower limits are consistent left and right. Integrating the right hand side of (3) is straightforward. The foolproof way of handling the left hand side of (3) is to write the variable as $1/[\mathrm{I}]^2$ as a numerator $[\mathrm{I}]^{-2}$ which integrates to (4) the indefinite integral and then (5) the definite integral. We tidy up (5) by multiplying by minus one to give the integrated second-order rate law.

$$\frac{1}{[\mathrm{I}]} - \frac{1}{[\mathrm{I}]_0} = k\,t$$ Integrated second-order rate law

$$(6)\quad \frac{1}{[\mathrm{I}]} - \frac{1}{6.72\times10^{-3}\,\mathrm{mol\,L^{-1}}} = (7.0\times10^{9}\,\mathrm{L\,mol^{-1}s^{-1}})(1.5\,\mathrm{s})$$

$$(7)\quad \frac{1}{[\mathrm{I}]} - (1.4881\times10^{2}\,\mathrm{L\,mol^{-1}}) = 1.05\times10^{10}\,\mathrm{L\,mol^{-1}}$$

$$(8)\quad \frac{1}{[\mathrm{I}]} = 1.050\times10^{10}\,\mathrm{L\,mol^{-1}} \qquad (9)\quad [\mathrm{I}] = 9.5238\times10^{-11}\,\mathrm{mol\,L^{-1}}$$

In (6) we substitute the physical quantities including the units for the variable of the integrated second-order rate equation. After 1.5 s the concentration of I-atoms has dropped from the original 6.72×10^{-3} to 9.5238×10^{-11} mol L^{-1} which is a negligible concentration. So the recombination of the iodine atoms at room temperature is a very rapid reaction.

Return to Question 1 (see page 37)

3.3.2 SOLUTION 2: BEER-LAMBERT LAW AND THE ABSORPTION OF LIGHT BY MOLECULES

$$(1)\quad -\frac{\mathrm{d}\,I}{\mathrm{d}\,x} = \kappa I[\mathrm{A}] \qquad (2)\quad \int_{I=I_0}^{I=I} \frac{\mathrm{d}\,I}{I} = -\kappa[\mathrm{A}] \int_{x=0}^{x=l} \mathrm{d}\,x$$

$$(3)\quad [\ln I]_{I=I_0}^{I=I} = -\kappa[\mathrm{A}]\,[x]_{x=0}^{x=l} \qquad (4)\quad \ln I - \ln I_0 = -\kappa[\mathrm{A}](l-0)$$

$$(4)\quad \ln\frac{I}{I_0} = -\kappa[\mathrm{A}]l \qquad (6)\quad \log\frac{I}{I_0} = -\frac{\kappa[\mathrm{A}]l}{2.303}$$

Equation (1) is the first-order ordinary differential equation for light absorption. Using the separation of variables method this is integrated in (2) using the boundary condition of the original light intensity $I = I_0$ at $x = 0$ to the total length of the optical cell $I = I$ at $x = l$ to give the integral (3). We substitute the limits in (4). The subtraction of two logs is replaced by the log of the ratio in (5) of light intensities. A more intuitive way of expressing the large range of absorption that different molecules may have (or a single molecule at different wavelengths may have) is to use logs to the base 10. To convert from natural log to log to the base 10 make use of $2.303 = \ln(x)/\log(x)$ as in (6) (Parker 2018, section 3.1.4). Equation (6) is tidied up by replacing kappa divided by 2.303 by the variable epsilon and by inverting the log function which removes the minus sign to give the Beer-Lambert law. The molar absorption coefficient ε has units of L mol^{-1} cm^{-1} as the length of the optical cell is in centimetres. For a particular molecule the absorption coefficient ε is wavelength dependent.

$$\log\frac{I_0}{I} = \varepsilon[\mathrm{A}]l \quad \text{Beer-Lamber law}$$

We may now calculate the concentration of chlorophyll-*a* in our solution as 1.5% of the incident light is transmitted at 417.8 nm through a 1 cm length cell and ε = 111700 L mol^{-1} cm^{-1} at 417.8 nm for chlorophyll-*a*. Make sure you type in your calculator log(100/1.5) in step (7) and not incorrectly log100/1.5 without the brackets.

$$(7)\quad \log(100/1.5) = (1.117\times10^5\,\mathrm{L\,mol^{-1}\,cm^{-1}})[\mathrm{A}](1.0\,\mathrm{cm})$$

$$(8)\quad 1.8239 = (1.117\times10^5\,\mathrm{L\,mol^{-1}})[\mathrm{A}]$$

$$(9)\quad [\mathrm{A}] = 1.6329\times10^{-5}\ \mathrm{mol\ L^{-1}}$$

Notice how strongly the chlorophyll-*a* absorbs at this wavelength with 98.5% light absorbed for such a dilute solution of ~10^{-5} mol L^{-1}.

Return to Question 2 (see page 38)

3.3.3 SOLUTION 3: DIFFUSION OF MOLECULES IN LIQUIDS, GASES OR SOLIDS

$$(1)\quad J = -D\frac{\mathrm{d}c}{\mathrm{d}x} \qquad (2)\quad J = \frac{1}{A}\frac{\mathrm{d}n}{\mathrm{d}t} \qquad (3)\quad \frac{\mathrm{d}n}{\mathrm{d}t} = -DA\frac{\mathrm{d}c}{\mathrm{d}x}$$

In Fick's first law of diffusion (1) the flux of molecules J mol m^{-2} s^{-1} is defined as (2) which is the number of moles diffusing per unit area and per unit time. So Fick's law may be rewritten as (3).

$$(4)\quad \frac{\mathrm{d}n}{\mathrm{d}t} = -DA\frac{\mathrm{d}c}{\mathrm{d}x} = -(0.522\times10^{-9}\ \mathrm{m^2 s^{-1}})(2.4\times10^{-6}\mathrm{m^2})\left(-\frac{100\ \mathrm{mol\ m^{-3}}}{1.5\times10^{-6}\ \mathrm{m}}\right)$$

$$(5)\quad \frac{\mathrm{d}n}{\mathrm{d}t} = 8.352\times10^{-8}\ \mathrm{mol\ s^{-1}} \qquad (6)\quad \mathrm{d}n = (8.352\times10^{-8}\mathrm{mol\ s^{-1}})\mathrm{d}t$$

$$(7)\quad \mathrm{d}n = (8.352\times10^{-8}\mathrm{mol\ s^{-1}})(600\,\mathrm{s}) \qquad (8)\quad \mathrm{d}n = 5.0112\times10^{-5}\ \mathrm{mol}$$

For the units to cancel in (4) we need to convert litres into metres cubed. As 1 L = 1 dm^3 so we must cube both the number and the unit to get the conversion factor 1 L = (0.1 m)^3 which is 1 L = 10^{-3} m^3. The concentration difference of the two sucrose solutions is converted to mol m^3 as follows. Concentration 0.1 mol L^{-1} = (0.1 mol L^{-1}) × (1 L/10^{-3} m^3) = 100 mol m^3. Remember the concentration gradient is negative.

The number of moles of sucrose passing through the 1.5 micron thick membrane in 10 minutes (600 s) is found using the separation of variables of the derivative from (5) through to (8). Note that the rate of diffusion of sucrose molecules (Fig. 3.5) is slow.

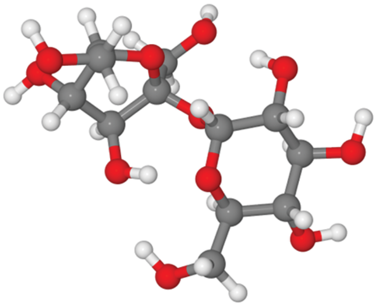

Figure 3.5: sucrose red O, dark grey C, grey H.

The net average distance moved by our sucrose molecules in 10 minutes is calculated above. Even though a sucrose molecule has a speed of 100s of metres per second, the random-walk (the collisions) means that the overall diffusion distance is on average about 0.8 mm in 10 minutes in water at 20 °C. The process of diffusion and mixing of solutions is a slow process.

$$<\Delta x^2>^{\frac{1}{2}} = \sqrt{2Dt} = \sqrt{2(0.522\times10^{-9}\ \mathrm{m^2 s^{-1}})(600\ \mathrm{s})} = 7.9145\times10^{-4}\ \mathrm{m}$$

Return to Question 3 (see page 40)

3.3.4 SOLUTION 4: THE AVERAGE SPEED OF GAS MOLECULES

Most chemistry textbooks gloss over this integration but it is not complicated. We are going to look at it in detail, because if you can do this integration, then you are well equipped to handle any other integration that you come across.

$$(1)\quad <c> = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \int_{c=0}^{c=\infty} c^3 e^{-Mc^2/2RT}\,dc$$

$$(2)\quad \overbrace{\int_{c=0}^{c=\infty}}^{\text{let } u=c^2 \text{ and } du=2c\,dc} c^3 e^{-ac^2}\,dc \qquad (3)\quad \int_{u=0}^{u=\infty} \frac{u}{2} e^{-au}\,du$$

Equation (1) is the average speed $<c>$ of gas molecules obtained from the Maxwell-Boltzmann speed distribution. Let's concentrate on the integral itself for the moment and write it as (2). For clarity in (2) let a be equal to the constants in the exponential $a = M/2RT$. (2) is the integral of a product of c^3 and $\exp(-ac^2)$ and let $u = c^2$ then $du = 2c\ dc$ which on substitution gives (3). Note that the limits have changed with the change of variable.

We have previously met the integration by parts using the tabular method (Parker 2018, section 8.1.3). We set up the table below with two rows. In row A each term is the differential of the preceding term and in row B each term is the integral of the preceding term. The terms are colour coded for clarity in the next step of the integration by parts.

A	$\mathrm{d}/\mathrm{d}u$	$\frac{u}{2}$	$\frac{1}{2}$	0
B	$\int \mathrm{d}u$	e^{-au}	$\frac{-\mathrm{e}^{-au}}{a}$	$\frac{\mathrm{e}^{-au}}{a^2}$

$$(4)\quad \int_{u=0}^{u=\infty} \frac{u}{2}\mathrm{e}^{-au}\,\mathrm{d}u = \left[+\left(-\frac{u}{2a}\mathrm{e}^{-au}\right)-\left(\frac{1}{2a^2}\mathrm{e}^{-au}\right)+C\right]_{u=0}^{u=\infty}$$

$$(5)\quad \int_{u=0}^{u=\infty} \frac{u}{2}\mathrm{e}^{-au}\,\mathrm{d}u = \left[\left(-\frac{u}{2a}-\frac{1}{2a^2}\right)\mathrm{e}^{-au}+C\right]_{u=0}^{u=\infty}$$

$$(6)\quad \int_{u=0}^{u=\infty} \frac{u}{2}\mathrm{e}^{-au}\,\mathrm{d}u = 0-\left(0-\frac{1}{2a^2}\right)=\frac{1}{2a^2}$$

In (4) we pair the first entry of row A (red) with the second entry of row B (red); then the second entry of row A (blue) with the third entry of row B (blue) and so on alternating the signs starting with a positive sign and carry on until the product of the pairing is zero. In (5) we clean up the equation and take the common exponential term outside the brackets. (6) Substitute the two limits, when $u = \infty$, $\exp(-au) = 0$, and when $u = 0$, $\exp(-au) = 1$ gives us the definite integral part of the Maxwell-Boltzmann average speed of gas molecules as $1/2a^2$.

$$(7)\quad <c> = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_{c=0}^{c=\infty} c^3\mathrm{e}^{-Mc^2/2RT}\,\mathrm{d}c$$

$$(8)\quad <c> = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\frac{1}{2a^2} \qquad \textbf{and } \boldsymbol{a=\frac{M}{2RT}}$$

$$(9)\quad <c> = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\frac{2R^2T^2}{M^2}$$

$$(10)\quad <c> = \frac{2^2\pi M^{3/2}2R^2T^2}{2^{3/2}\pi^{3/2}R^{3/2}T^{3/2}M^2}$$

The integral part of the average speed $1/2a^2$ is substituted in (7) to give (8). In (8) we substitute a with $M/2RT$ to obtain (9). To tidy up (10) the various powers are written individually and then bring each variable to a single power. Our integration by parts has given us the Maxwell-Boltzmann average speed of gas molecules below which is a remarkably simple result. The average speed depends upon the mass of the molecule and the temperature but not the nature of the molecules, *i.e.* it is treated as an ideal gas.

$$<c> = \left(\frac{8RT}{\pi M}\right)^{1/2} \qquad \text{Maxwell-Boltzmann average speed of gas molecules}$$

The definition of the average speed $<c>$ is that there are the same number of molecules with less than the average speed as there are with more than the average speed. In Fig. 3.6 the equal areas under the curve are colour coded for clarity. The most probable speed $c_{\mathrm{mp}} = (2RT/M)^{1/2}$ is the maximum of the speed distribution curve. The average speed $<c>$ is greater than the most probable speed due to the distribution being skewed towards high speeds.

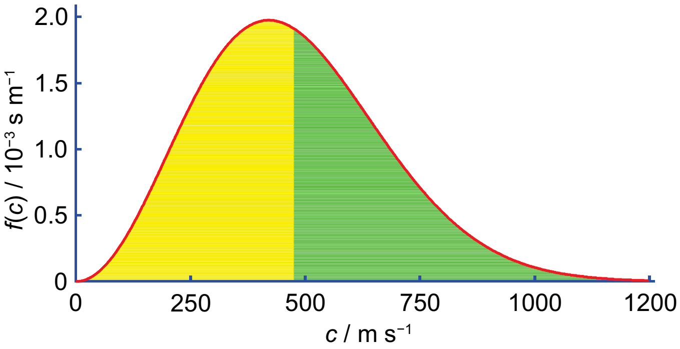

Figure 3.6: Maxwell-Boltzmann speed distribution for N_2 at 298.15 K.

The average speed and the most probable speed for N_2 at 298.15 K are calculated below. Although the average speed of the N_2 molecule is very large, about half a kilometre a second, because of diffusion (section 3.2.3), the average distance travelled by a N_2 molecule is only 5.5 millimetres per second at ambient temperatures and pressures (the diffusion constant for N_2 is $D = 1.5\times10^{-5}$ m^2 s^{-1}).

$$<c> = \left(\frac{8\,RT}{\pi\,M}\right)^{1/2} = \left(\frac{8\left(8.3141\ \mathrm{J\,K^{-1}mol^{-1}}\right)\left(298.15\ \mathrm{K}\right)}{\pi\left(28.02\times10^{-3}\ \mathrm{kg\ mol^{-1}}\right)}\right)^{1/2} = 474.6\,\mathrm{m\ s^{-1}}$$

$$c_{\mathrm{mp}} = \left(\frac{2\,RT}{M}\right)^{1/2} = \left(\frac{2\left(8.3141\ \mathrm{J\,K^{-1}mol^{-1}}\right)\left(298.15\ \mathrm{K}\right)}{28.02\times10^{-3}\ \mathrm{kg\ mol^{-1}}}\right)^{1/2} = 420.6\,\mathrm{m\ s^{-1}}$$

The units cancel in the above calculation when in the SI base units, and the SI unit of mass is the kg not the gram. Remember the definitions of force and work (or energy) with the two named units newton and joule, respectively.

$$\mathrm{J} = \overbrace{\text{work or energy}}^{\text{joule}} = \overbrace{\text{force}}^{\text{newton}} \times\text{distance} = \overbrace{\text{mass}\times\text{acceleration}}^{\text{newton}}\times\text{distance} = \mathrm{kg\ m^2\ s^{-2}}$$

Return to Question 4 (see page 41)

4 WEEK 4: CHEMISTRY & SECOND-ORDER ORDINARY DIFFERENTIAL EQUATIONS

This week we are concentrating on second-order ODEs (Section 3.1.2). Second-order ordinary differential equations are common in quantum mechanics (also called wave mechanics).

$$-\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi=E\psi$$ Schrödinger equation for motion in one-dimension

The Schrödinger equation describes the wavefunction ψ for a particle of mass m (kg per particle) moving in one-dimension '1-D'. Particle is the general term for photon, electron, atom, molecule, or ion. The wavefunction ψ (psi) is related to the probability of the molecule being at a position x. The wavefunction ψ varies with the position x so should really be written $\psi(x)$ but for clarity I have written it just as ψ. $V(x)$ is the potential energy of the particle as a function of its position in the one-dimension x. E is the total energy of the particle (the sum of the potential and the kinetic energy) and is constant for an isolated system, h is Planck's constant. Sometimes you will see the symbol $\hbar$ (pronounced 'haitch cross') where $\hbar = h/2\pi$ is Planck's constant divided by 2π.

Solving a second-order differential equation requires that we know two boundary conditions, which might be in our example, the values of ψ at the two ends of the one-dimension box $x = 0$ and $x = L$. We will solve some simple second-order differential equations (Schrödinger equations).

4.1 WEEK 4 TUTORIAL QUESTIONS

4.1.1 QUESTION 1: UNCONSTRAINED MOVEMENT OF A MOLECULE IN ONE-DIMENSION

Consider the free motion of a molecule moving in 'infinitely' large space, that is infinitely large compared with the size of the molecule, so a container of macroscopic size would be 'infinitely' large compared with the size of the molecule.

$$\frac{-h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi$$

In our question we have free motion (unconstrained) which means that the molecule is not subjected to any external forces. As the molecule experiences no forces the potential energy $V(x)$ must be constant and we are free to define its value. If we let $V(x) = 0$ then the Schrödinger equation above is simplified.

$$\frac{-h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi$$

If our molecule of mass m is moving at velocity v in one-dimension x then the general equation for its wavefunction is shown below.

$$\psi = A\sin\left(\frac{2\pi m v}{h}x\right) + B\cos\left(\frac{2\pi m v}{h}x\right) \quad \text{General wavefunction for 1-D motion}$$

Using the general wavefunction for a molecule in 1-D solve the second-order ODE Schrödinger equation and find the total energy E of our molecule moving unconstrained by forces in one-dimension. What can you deduce from your solution of the quantum mechanics of the free motion in infinite space of a particle (a molecule in our example).

Jump to Solution 1 (see page 56)

4.1.2 QUESTION 2: MOVEMENT OF A PARTICLE IN A ONE-DIMENSIONAL BOX

We have just looked at the unconstrained motion of a particle due to it having infinite boundaries, what we consider next is the particle constrained by boundaries.

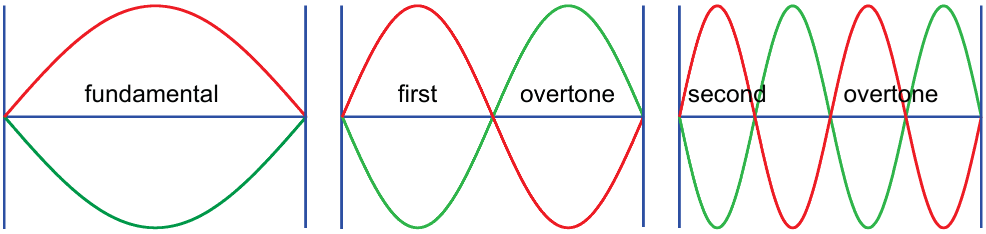

Figure 4.1: the three lowest standing waves of a stretched string.

The simplest example of a standing wave is a stretched string, as in a guitar string where one end of the string is held fixed by the 'saddle' and the other by the frets and fingers, so this is one-dimensional problem. Plucking the string (Fig. 4.1) causes the string to vibrate with fixed or resonant frequencies (standing waves) between the peak amplitude Fig. 4.1 red, and the trough amplitude green. These standing wave vibrations are the ones you can hear from a string instrument (guitar, violin, or piano). The lowest vibration is the 'fundamental' with half a wavelength equal to the length of the string. The next two standing waves of higher energies are with one complete wavelength and two complete wavelengths equal to the length of the string, the 'first overtone' and 'second overtone'. In order to be a standing wave the wave does not move through space from left to right but it continually oscillates up and down between the peak amplitude (red) and the trough amplitude (green in Fig. 4.1).

Standing waves are 'quantized' and standing waves are important in quantum mechanics (as well as music) because they are the waves which persist though time and can thus be detected as physical quantities. When we consider particles confined in atoms, molecules, a 1-D box (section 4.1.2), a 2-D box (section 1.2.1), or a 3-D box then the wavefunctions have to be standing waves in order to persist through time and be detected as physical events.

An example of confinement in a 1-D box is the motion of the mobile π-electrons in a conjugated polyene molecule (Parker 2018, section 2.1.10). Fig. 4.2 shows a short polyene molecule.

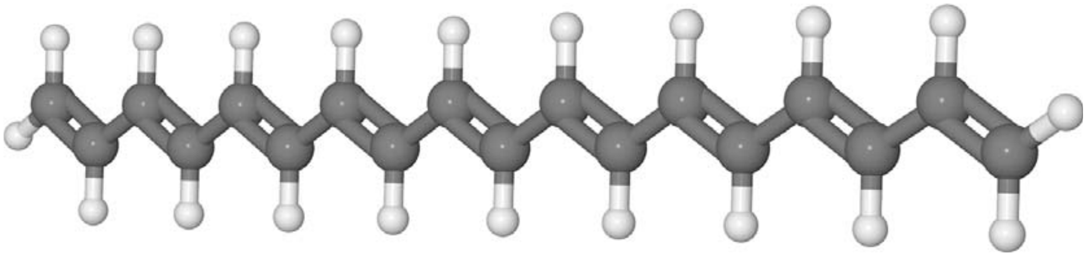

Figure 4.2: polyene molecule. dark grey C, grey H.

In general we may visualize the one-dimensional box which is of molecular size as below.

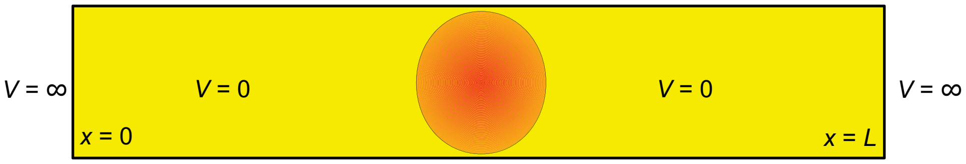

Figure 4.2: a particle confined a one-dimensional box.

For the particle confined to a one-dimensional box we use the Schrödinger equation in one-dimension.

$$\frac{-h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi$$

The potential energy inside the box is constant and is infinite outside the box, hence confining the particle inside the box. We may choose the value for the constant potential in the box and choosing $V(x) = 0$ will simplify the Schrödinger equation.

$$\frac{-h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi$$

Outside the box the potential energy is infinite so the particle cannot escape from the box. The walls at the beginning and end of the box define the two boundary conditions that we need in order to solve our second-order ordinary differential equation. The wavefunction must be equal to zero $\psi(0) = 0$ and $\psi(L) = 0$ at the two boundaries in order for the wave to 'reflect' at the walls exactly, so the wavefunction is a standing wave and can persist through time. Quantum mechanics gives the trial wavefunction below (Parker 2018, section 8.2.2).

$$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \quad \text{Wavefunction of a particle confined in a 1-D box}$$

Where $n = 1, 2, 3, 3\ldots$ are the quantum numbers for the translational motion in one-dimension. First, solve the first-order ordinary differential equation, the one-dimensional Schrödinger equation, by calculating the allowed energy levels using the trial wavefunction and the boundary conditions. Secondly, sketch the shapes of the first few allowed wavefunctions using a spreadsheet.

Jump to Solution 2 (see page 57)

4.1.3 QUESTION 3: MOTION OF A PARTICLE ON A RING

Rotational motion in two-dimensions is exemplified with the circular motion of a particle moving on a ring. To a first approximation we may treat the π-electrons in benzene as particles on a ring, where we treat the carbon atoms of the regular hexagon of benzene as a circle.

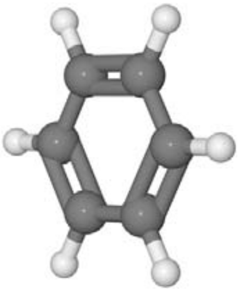

Figure 4.3: benzene, dark grey C, grey H.

The wavefunction for the π-electrons of benzene must satisfy a cyclic boundary condition that the wavelengths must fit exactly into the circumference in order for them to be standing waves, there must be an integral number of wavelengths in the circumference, Fig. 4.4.

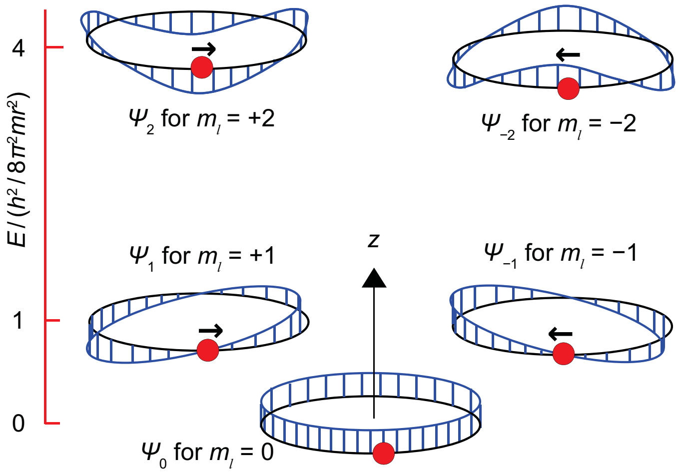

Figure 4.4: wavefunctions (blue) for a particle (red) on a ring (black).

The wavefunction ψ_0 has a uniform amplitude around the ring, the particle is stationary and not rotating around the ring. The particle has the same probability of being found anywhere on the ring and from Heisenberg's uncertainty principle we cannot locate the particle's position on the ring. For ψ_1 and ψ_{-1} there is one complete wavelength fitting the circumference, and for ψ_2 and ψ_{-2} two complete wavelengths fitting the circumference. The cyclic boundary condition of an integral number of wavelengths fitting the circumference of the ring is shown below.

$$m_l\lambda = 2\pi r \qquad m_l = 0, \pm 1, \pm 2, \pm 3\ldots \qquad \text{Particle on a ring boundary condition}$$

By convention the quantum number for rotational motion has the symbol m_l (don't confuse this m for the mass of the particle). The plus and minus values for m_l are for the particle moving clockwise or anti-clockwise around the ring when viewed looking in the direction of the axis of rotation (the z-axis). However, changing the direction of rotation (positive or negative values of m_l) does not change the energy of the wavefunction although it changes the shape of the wavefunction (they are degenerate).

$$(1)\quad \psi = A\sin\left(\frac{2\pi}{\lambda}x\right) + B\cos\left(\frac{2\pi}{\lambda}x\right) \qquad (2)\quad \psi = A\sin\left(\frac{m_l}{r}x\right) + B\cos\left(\frac{m_l}{r}x\right)$$

$$(3)\quad -\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi \qquad (4)\quad -\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi$$

The general equation for a wave on a ring is (1) where x is the distance around the circumference. The cyclic boundary condition rearranges to $2\pi/\lambda = m_l/r$ which gives us the standing quantized wavefunction (2) for the benzene π-electrons. In the Schrödinger equation (3) the potential energy for the π-electrons is constant around the ring, and thus we may set it equal to zero $V(x) = 0$ as in (4).

Solve the second-order ODE of the Schrödinger equation (4) using the wavefunction (2) and find the equation for the allowed quantized energies for the particle on a ring.

Jump to Solution 3 (see page 59)

4.1.4 QUESTION 4: MOTION OF A PARTICLE ON A RING, THE ABSORPTION SPECTRUM OF BENZENE

Continuing the ideas developed in question 3 as benzene has 6 π-electrons and applying Pauli's exclusion principle there will be 2 π-electrons in $m_l = 0$ with 2 π-electrons in $m_l = -1$ and 2 π-electrons in $m_l = +1$. The highest occupied molecular orbitals (HOMOs) are the degenerate $m_l = \pm 1$ pair. The lowest unoccupied molecular orbitals (LUMOs) are the degenerate $m_l = \pm 2$ pair, Fig. 4.5.

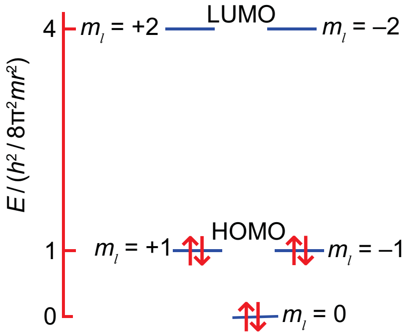

Figure 4.5: benzene π-electron energies for the particle on a ring model.

The C-C bond distance in benzene is 1.40 Å and so for the regular hexagon the radius of the ring in our quantum treatment is r = 1.40 Å.

Calculate the wavelength of light absorbed to excite the transition from $m_l = \pm 1$ to $m_l = \pm 2$, using the allowed energy equation that you derived in section 4.2.3 and also the energy of a photon of light and the wavelength of the light absorbed using the equations below.

$$E_{\text{photon}} = h\nu \qquad c = \lambda\nu$$

Jump to Solution 4 (see page 61)

4.2 WEEK 4 TUTORIAL SOLUTIONS

4.2.1 SOLUTION 1: UNCONSTRAINED MOVEMENT OF A MOLECULE IN ONE-DIMENSION

$$(1) \quad \psi = A\sin\left(\frac{2\pi m v}{h}x\right) + B\cos\left(\frac{2\pi m v}{h}x\right)$$

$$(2) \quad \frac{d\psi}{dx} = A\left(\frac{2\pi m v}{h}\right)\cos\left(\frac{2\pi m v}{h}x\right) - B\left(\frac{2\pi m v}{h}\right)\sin\left(\frac{2\pi m v}{h}x\right)$$

$$(3) \quad \frac{d^2\psi}{dx^2} = -A\left(\frac{2\pi m v}{h}\right)^2\sin\left(\frac{2\pi m v}{h}x\right) - B\left(\frac{2\pi m v}{h}\right)^2\cos\left(\frac{2\pi m v}{h}x\right)$$

$$(4) \quad \frac{d^2\psi}{dx^2} = -\left(\frac{2\pi m v}{h}\right)^2\overbrace{\left(A\sin\left(\frac{2\pi m v}{h}x\right) + B\cos\left(\frac{2\pi m v}{h}x\right)\right)}^{\textbf{wavefunction } \psi}$$

From the general wave equation (1) for a particle of mass m and velocity v we can calculate the first derivative (2), then the second derivative (3). In (3) we move the common factor outside brackets to give (4). The terms in (4) involving the sine and cosine functions are the same as the wavefunction ψ, thus the second derivative (4) becomes (5).

$$(5)\quad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\left(\frac{2\pi m v}{h}\right)^2 \psi \qquad (6)\quad -\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi$$

$$(7)\quad \frac{h^2}{8\pi^2 m}\left(\frac{2\pi m v}{h}\right)^2 \overset{\text{cancel}}{\psi} = E\overset{\text{cancel}}{\psi} \qquad (8)\quad E = \frac{h^2}{8\pi^2 m}\left(\frac{2\pi m v}{h}\right)^2$$

We now substitute the second derivative (5) into the Schrödinger equation (6) with $V(\psi) = 0$. The two wavefunctions ψ in (7) cancel. The total energy (8) E is equal to the translational energy as the potential energy is defined as zero. In (8) we can cancel out terms to give the total energy of unconstrained motion in one-dimension of infinite size as shown below.

$E = \frac{1}{2}mv^2$ Quantum mechanics energy of the unconstrained motion of a particle

The unconstrained motion of the molecule has the same energy as the classical Newtonian translational energy and is non-quantized. This is another example of the 'correspondence principle' (section 2.2.2).

It is the presence of the 'boundary conditions' which leads to the quantization and if the one-dimensional motion is 'infinite' compared to the size of a molecule and also field-free it does not have any boundary and hence cannot have any boundary conditions.

Return to Question 1 (see page 50)

4.2.2 SOLUTION 2: MOVEMENT OF A PARTICLE IN A ONE-DIMENSIONAL BOX

$$(1)\quad \psi = \left(\frac{2}{L}\right)^{1/2}\sin\frac{n\pi x}{L} \qquad (2)\quad \frac{\mathrm{d}\psi}{\mathrm{d}x} = \left(\frac{n\pi}{L}\right)\left(\frac{2}{L}\right)^{1/2}\cos\frac{n\pi x}{L}$$

$$(3)\quad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\left(\frac{n\pi}{L}\right)^2 \overbrace{\left(\frac{2}{L}\right)^{1/2}\sin\frac{n\pi x}{L}}^{\textbf{wavefunction}\,\psi} \qquad (4)\quad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\left(\frac{n\pi}{L}\right)^2\psi$$

The wavefunction for a particle in a one-dimensional box (1) is differentiated in (2) and the second derivative is taken in (3). Part of the right hand side of (3) is recognisable as our initial wavefunction, substitution of which gives the second derivative as (4).

$$(5)\quad -\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \qquad (6)\quad -\frac{h^2}{8\pi^2 m}\left(-\left(\frac{n\pi}{L}\right)^2\psi\right) = E\psi$$

$$(6)\quad \frac{n^2 h^2 \pi^2}{8\pi^2 m L^2}\psi = E\psi$$

We can now substitute our second derivative of the wavefunction (4) back into the Schrödinger equation with zero potential energy (5) to get (6). In (7) Cancelling the red terms gives the quantized energy levels of a particle in a one-dimensional box.

$$E = \frac{n^2 h^2}{8 m L^2} \qquad \overbrace{n = 1, 2, 3 \ldots}^{\textbf{quantum numbers}}$$

Quantized energy levels for a particle in a 1D box

These are the allowed energy levels. This 'bounded' motion has quantized solutions whereas the 'unbounded' motion of section 4.2.1 resulted in the classical Newtonian energy $E = ½mv^2$ which is continuous and not quantized. Quantization is the result of our particle having a confined motion. Below are the lowest two allowed wavefunctions for $n = 1$ and $n = 2$.

$$\psi_1 = \sqrt{\frac{2}{L}}\,\sin\overbrace{\left(\frac{\pi x}{L}\right)}^{n=1} \qquad \psi_2 = \sqrt{\frac{2}{L}}\,\sin\overbrace{\left(\frac{2\pi x}{L}\right)}^{n=2}$$

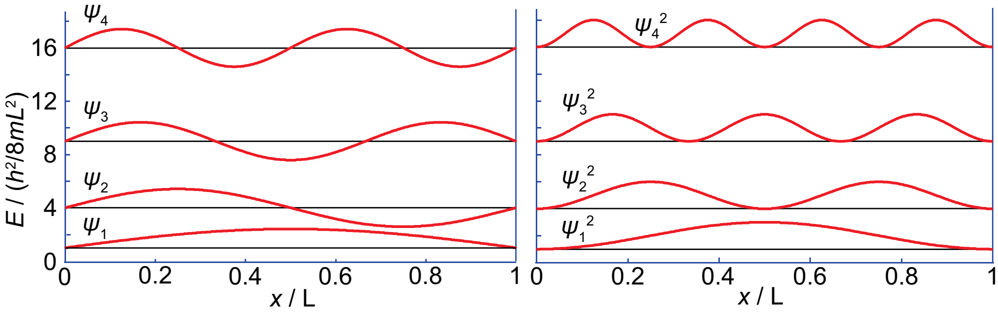

Figure 4.6: particle in a 1-D box, wavefunctions (left), probability densities (right).

Fig. 4.6 plots the four lowest wavefunctions and the probability density of finding the particle at a given position (the square of the wavefunction) these plots are a good exercise in using a spreadsheet. The wavefunctions (left) are the standing waves for the particle in the one-dimensional box. The allowed quantized total energies (black) are constant and don't vary with the position of the particle in the box (they are horizontal), but E_1 to E_4 increase as n^2.

Fig. 4.6 for $n = 1$ there is one maximum for the probability density in the middle of the box. The probability density for $n = 2$ has two maxima. For very high quantum numbers there are a large number of maxima and the probability density becomes evenly spread over the length of the box. In the limit the behaviour becomes classical, this is another example of the 'correspondence principle' (section 2.2.2).

Return to Question 2 (see page 51)

4.2.3 SOLUTION 3: MOTION OF A PARTICLE ON A RING

$$(1)\quad \psi = A\sin\frac{m_l x}{r} + B\cos\frac{m_l x}{r}$$

$$(2)\quad \frac{\mathrm{d}\psi}{\mathrm{d}x} = A\frac{m_l}{r}\cos\frac{m_l x}{r} - B\frac{m_l}{r}\sin\frac{m_l x}{r}$$

$$(3)\quad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -A\left(\frac{m_l}{r}\right)^2\sin\frac{m_l x}{r} - B\left(\frac{m_l}{r}\right)^2\cos\frac{m_l x}{r}$$

$$(4)\quad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\left(\frac{m_l}{r}\right)^2\overbrace{\left(A\sin\frac{m_l x}{r} + B\cos\frac{m_l x}{r}\right)}^{\text{wavefunction }\psi}$$

(1) is the wavefunction with the boundary condition that only an integral number of waves can fit in the circumference for the wave to be a standing wave. The first derivative is (2) and the second derivative is (3). The second derivative (3) is cleaned up in (4) and note that the right hand bracket can be replaced with the wavefunction to give (5).

$$(5)\quad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\left(\frac{m_l}{r}\right)^2\psi \qquad (6)\quad \overbrace{-\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi}^{\text{Schrodinger equation } V=0}$$

$$(7)\quad -\frac{h^2}{8\pi^2 m}\left(-\frac{m_l^2}{r^2}\right)\overset{\text{cancel}}{\psi} = E\overset{\text{cancel}}{\psi}$$

The second derivative (5) is substituted into the Schrödinger equation (6) with a zero potential energy term to give (7). Cancelling out ψ in (7) leads to the quantized energy levels of the particle on a ring, which is a first approximation to the π-electron energies of benzene.

$$E = \frac{m_l^2 h^2}{8\pi^2 m r^2} \quad \text{Quantized energies of a particle on a ring}$$

Return to Question 3 (see page 53)

4.2.4 SOLUTION 4: MOTION OF A PARTICLE ON A RING, THE ABSORPTION SPECTRUM OF BENZENE

$$(1)\quad E_{m_l} = \frac{m_l^2 h^2}{8\pi^2 m r^2} \qquad (2)\quad E_{\pm 1} = \frac{h^2}{8\pi^2 m r^2} \qquad (3)\quad E_{\pm 2} = \frac{4h^2}{8\pi^2 m r^2}$$

$$(4)\quad \Delta E = \frac{3h^2}{8\pi^2 m r^2}$$

$$(5)\quad \Delta E = \frac{3\left(6.6261\times10^{-34}\ \text{J s}\right)^2}{8\pi^2\left(9.1094\times10^{-31}\ \text{kg}\right)\left(1.40\times10^{-10}\ \text{m}\right)^2} = 9.3433\times10^{-19}\ \text{J}$$

From section 4.2.2 the energy of the particle on a ring is (1). This allows us to calculate the energies of quantum levels for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in (2) and (3), respectively. The energy of the quantum jump (4) between these MOs may then have the physical quantities entered in (5). Notice how electronic energy levels are of the order 10^{-19} J which is a minute quantity of energy.

$$(6)\quad E = h\nu = 9.3433\times10^{-19}\ \text{J} \qquad (7)\quad \nu = \frac{9.3433\times10^{-19}\ \text{J}}{6.6261\times10^{-34}\ \text{J s}} = 1.4101\times10^{15}\ \text{s}^{-1}$$

$$(8)\quad \lambda = \frac{c}{\nu} = \frac{2.9979\times10^{8}\ \text{m s}^{-1}}{1.4101\times10^{15}\ \text{s}^{-1}} = 2.126\times10^{-7}\ \text{m} = 212.6\,\text{nm}$$

In order for the photon to be absorbed by the benzene molecule, the photon energy (6) must be the same as the difference between energy levels HOMO → LUMO. The frequency (7) of the absorbed light is of the order 10^{15} s^{-1} in the ultraviolet part of the spectrum. The wavelength of the light (8) in the conventional units of nanometres (nm) is 212.6 nm by this approximate treatment.

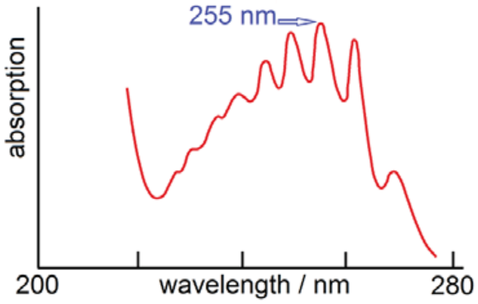

Figure 4.7: absorption spectrum of benzene vapour.

Fig. 4.7 shows that the experimental π to π^* absorption has $\lambda_{max} \approx 255$ nm, so the agreement is pretty good considering that this is our first approximation. To obtain better agreement with experimental results we need to use more advanced quantum chemistry approaches. In increasing levels of sophistication these are: Hückel, semi-empirical, ab initio, and DFT (density functional theory) methods. Within each method there are several levels of refinement. Nevertheless the particle on a ring has the advantage that it gives us a clear qualitative understanding of the π-electrons' molecular orbital structure for benzene and the degeneracy of the MOs.

Aromatic molecules are cyclic conjugated molecules. The particle on a ring treatment showed us that $n = 0$ is non-degenerate but for $n > 0$ the MOs are doubly degenerate and from Pauli's exclusion principal we need 2 electrons to fill each MO. The total number of π-electrons in an aromatic molecule is $2(2n+1)$ or $4n+2$ which is known as Hückel's rule.

Return to Question 4 (see page 55)

5 WEEK 5: CHEMISTRY AND ADVANCED INTEGRATION

This week's tutorials will use the three techniques of integration by substitution, integration by parts (see section 3.3.4) and integration using partial fractions.

5.1 WEEK 5 TUTORIAL QUESTIONS

5.1.1 QUESTION 1: DISSOLUTION OF A SOLID BY A SOLVENT

Dissolution of a solid is the process of forming a solution in a solvent. The crystal lattice breaks down so that the constituent of the crystal (ions, atoms or molecules) are transported into the solvent and become solvated. Dissolution is used in analytical chemistry, metal extraction from their ores, nuclear waste reprocessing, pharmaceutical manufacturing, chemical engineering and biological processes. Fig. 5.1 shows dissolution in a simple diagrammatic fashion.

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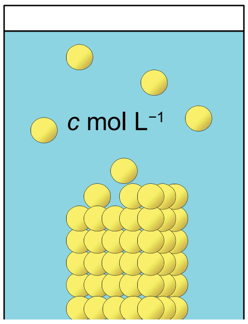


Figure 5.1: dissolution of a solid in a solvent.

The dissolution of a solid in a solvent is frequently controlled by diffusion. If the concentration of the saturated solution is c_s (a constant at a given temperature for a chosen solid-solvent pair) then the concentration of the solid in solution c after a time t is determined by the following integral.

$$\int_{c=0}^{c=c} \frac{1}{c_s - c}\,\mathrm{d}c = \int_{t=0}^{t=t} k\,\mathrm{d}t$$

Where k is a constant that indicates how fast the solid dissolves at a given temperature. Integrate by substitution to find the concentration c as a function of time t.

Jump to Solution 1 (see page 56)

5.1.2 QUESTION 2: POPULATION OF DIATOMIC MOLECULES IN ROTATIONAL QUANTUM LEVELS

Molecules move through space (called translational motion) and they also rotate and vibrate. Quantum mechanics shows us that the rotations and vibrations can only occur with quantized energy levels. Fig. 5.2 shows the rotation of an HCl molecule around its centre of gravity (centre of mass). For a linear molecule the random tumbling motion may be resolved into two components at right angle to one another, these are around the Cartesian x and y axes where z is the molecular axis. The molecule cannot rotate around the z axis as this motion is a spin and does not change the positions of the atoms, which is required in order to be a rotation, for the difference between spin and rotation see Parker 2015, section 1.7.6.

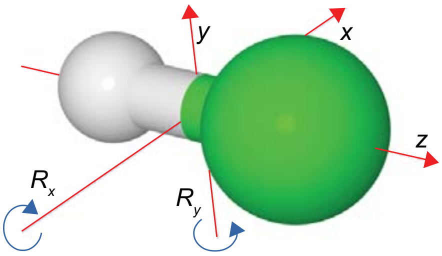


Figure 5.2: HCl axes and rotations, grey H and green Cl.

In order to calculate the population of diatomic molecules, such as HCl, in the various rotational energy levels you need to calculate something called the rotational partition function q^{R} (covered in the later years of your degree). The rotational partition function q^{R} is equal to the integral below.

$$q^{\mathrm{R}} = \int_{J=0}^{J=\infty} (2J+1)\, \mathrm{e}^{-J(J+1)h^2/(8\pi^2 I k_{\mathrm{B}} T)}\, \mathrm{d}J$$

Where for a given molecule: I is a constant called the 'moment of inertia', h is Planck's constant, k_{B} is Boltzmann's constant, and T is the absolute temperature. The rotational quantum number J can only have integer values of $J = 0, 1, 2, 3\ldots$ (that's the quantum mechanics bit). Although J is quantized and thus one would expect a summation to be used, the rotational energy levels are very closely spaced compared with thermal energy about $k_{\mathrm{B}}T$ and so it is a very good approximation to use integration instead of summation (and it is easier). Integration is carried out over all possible J values from zero to the theoretical upper limit of infinity. Calculate this integral by using the method of substitution, I suggest you use $z = J(J+1)$.

Jump to Solution 2 (see page 57)

5.1.3 QUESTION 3: CHEMISTRY AND RADIAL DISTRIBUTION FUNCTIONS

$$\psi_{1\mathrm{s}} = \frac{1}{\pi^{1/2} a_0^{3/2}}\, \mathrm{e}^{-r/a_0} \quad \text{H-atom 1s wavefunction}$$

In the wavefunction $\psi_{1\mathrm{s}}$ of an electron in the 1s atomic orbital of a hydrogen atom: a_0 is the Bohr radius 0.5292 Å the unit Å is an ångstrom equal to 10^{-10} m, and r is the distance of the electron from the nucleus. Notice that at the nucleus when $r = 0$ then $\psi_{1\mathrm{s}} = 1/(\pi^{1/2} a_{\mathrm{o}}^{3/2}) = 1.4655$ Å$^{2/3}$ a non-zero value.

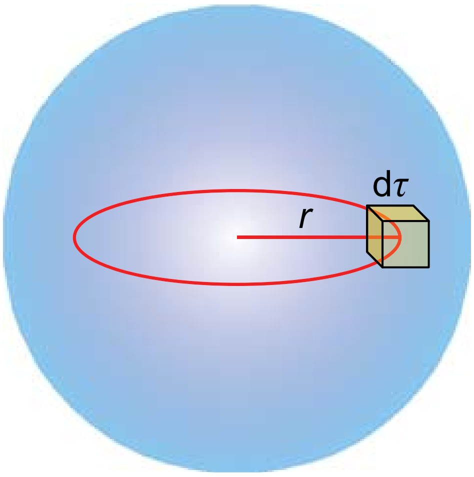


Figure 5.3: $\psi_{1s}{}^2 d\tau$ is the probability of an electron being in a cubic volume.

Fig. 5.3 the probability that the electron is in a small cubic volume of space dτ at a distance r from the nucleus is equal to the square of the wavefunction multiplied by the small volume $\psi_{1s}{}^2 d\tau$. If we divide $\psi_{1s}{}^2 d\tau$ by the small volume dτ we obtain the probability density (per unit volume) called the 'probability density' $\psi_{1s}{}^2$.

$$\psi_{1s}^2 = \frac{1}{\pi a_0{}^3} e^{-2r/a_0}$$ H-atom 1s probability density (per unit volume)

Note the $2r$ term in the exponential from squaring the wavefunction. For the spherically symmetric 1s wavefunction its probability density is 'one-dimensional' as it only depends upon the distance from the nucleus. The probability density has a non-zero value at the nucleus of $1/(\pi a_0{}^3)$ = 2.1478 Å^{-3} because the probability density is crammed into a small volume around the nucleus. So perhaps the concept of probability density is not very intuitive, however, there is a more intuitive approach.

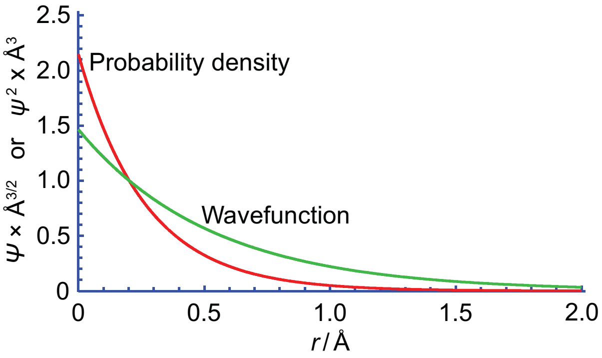


Figure 5.4: H-atom 1s wavefunction and probability density.

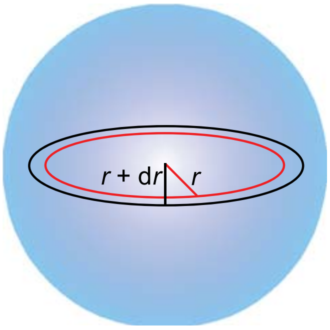


Figure 5.5: a cut through two concentric spheres.

Perhaps more readily grasped is probability of the electron being in a thin spherical shell between two concentric spheres which are at distances from the nucleus of r and $(r+dr)$.

(1) $$V(r+\mathrm{d}r)-V(r)=\frac{4}{3}\pi(r+\mathrm{d}r)^3-\frac{4}{3}\pi r^3$$

(2) $$V(r+\mathrm{d}r)-V(r)=\frac{4}{3}\pi(\boldsymbol{r^3}+3r^2\mathrm{d}r+\overbrace{3r\,\mathrm{d}r^2+\mathrm{d}r^3}^{\textbf{negligible}}-\boldsymbol{r^3})$$

(3) $$V(r+\mathrm{d}r)-V(r)=4\pi r^2\mathrm{d}r$$

The volume of the thin spherical shell is calculated in (1). In (2) the terms involving r-cubed in red cancel out and we can safely ignore the terms involving dr squared and cubed as they are negligibly small as dr is itself small. The volume of the thin shell (3) is $4\pi r^2 \mathrm{d}r$. The probability of the electron being in this shell is equal to $4\pi r^2 \psi_{1s}{}^2 \mathrm{d}r$. If we divide this probability by dr we obtain the probability density per unit distance known as the 'radial distribution function' $P(r)$.

$$P(r) = 4\pi r^2 \psi_{1s}^2 = \frac{4}{a_0^3} r^2 \mathrm{e}^{-2r/a_0}$$ H-atom 1s radial distribution function(probability density per unit distance)

The various functions and their names are summarized below for the example of the 1s H-atom.

wavefunction

$$(1) \quad \psi_{1s} = \sqrt{\frac{1}{\pi a_0^3}}\ \mathrm{e}^{-r/a_0}$$

probability density

$$(2) \quad \psi_{1s}{}^2 = \frac{1}{\pi a_0^3}\ \mathrm{e}^{-2r/a_0}$$

$$(3) \quad P_{1s}(r) = \frac{4}{a_0^3} r^2\, \mathrm{e}^{-2r/a_0}$$

radial distribution function

$$(4) \quad P_{1s}(r_1\text{-}r_2) = \frac{4}{a_0^3} \int_{r_1}^{r_2} r^2\, \mathrm{e}^{-2r/a_0}\, \mathrm{d}r$$

probability between r_1 and r_2

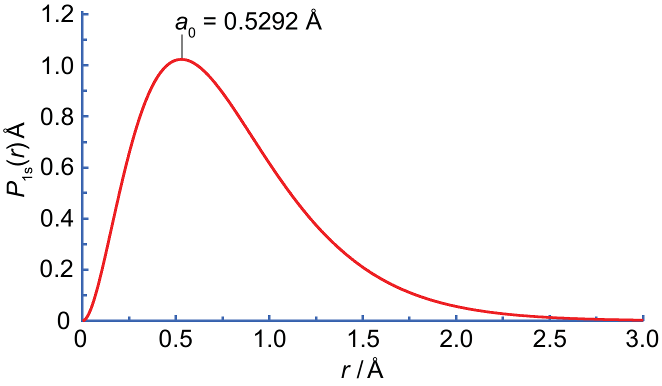


Figure 5.6: H-atom 1s radial distribution function.

Fig. 5.6 shows that the H-atom 1s radial distribution function is skewed towards high values of the radius due to the r^2 term which also makes the radial distribution function zero at the nucleus. The most likely radius for electron is at the maximum called the Bohr radius a_0 = 0.5292 Å.

The average value of the radius $<r_{1s}>$ is obtained from the integral of r multiplied by the radial distribution function as below. Calculate the average distance from the nucleus for the 1s H-atom electron.

$$<r_{1s}> = \frac{4}{a_0^3} \int_{r=0}^{r=\infty} r^3 \mathrm{e}^{-2r/a_0} \mathrm{d}r$$ Average distance of a 1s H-atom electron from the nucleus

Jump to Solution 3 (see page 75)

5.1.4 QUESTION 4: COMPUTATIONAL CHEMISTRY

$$I_0 = \int_{r=0}^{r=\infty} \mathrm{e}^{-ar^2}\,\mathrm{d}r = \frac{1}{2}\sqrt{\frac{\pi}{a}} \qquad I_1 = \int_{r=0}^{r=\infty} r\,\mathrm{e}^{-ar^2}\,\mathrm{d}r \qquad I_2 = \int_{r=0}^{r=\infty} r^2\,\mathrm{e}^{-ar^2}\,\mathrm{d}r$$

The integral I_0 is a standard integral, it is also the first of a series of integrals called 'Gaussian integrals' the next two members of the Gaussian integrals are I_1 and I_2.

Gaussian integrals are important in computational chemistry in finding approximate numerical solutions to the Schrödinger equation of molecular wavefunctions. Such quantum chemistry calculations model not only molecular structures but chemical reaction profiles and thermodynamic properties and are widely used in chemical, biological, and pharmaceutical research both in industry and in universities, eg the structure and interactions of enzyme molecules with their target sites. Since the exact molecular orbitals of large molecules are highly complex, they are approximated by 'Gaussian wavefunctions' that all contain the $r^n \times \exp(-ar^2)$ where the power n is an integer. These Gaussian integrals are much easier to integrate than wavefunctions and they give good approximations to molecular orbital wavefunctions.

Calculate the integral I_1 using the substitution method. Integrate I_2 using integration by parts and the substitution method.

Jump to Solution 4 (see page 77)

5.1.5 QUESTION 5: SPECTROSCOPY AND FOURIER TRANSFORM

The techniques of Raman, infrared, UV-visible and microwave spectroscopy normally use a Michelson interferometer to measure an interferogram (Harris 2007, p 442, and Hollas 2004, p 48).

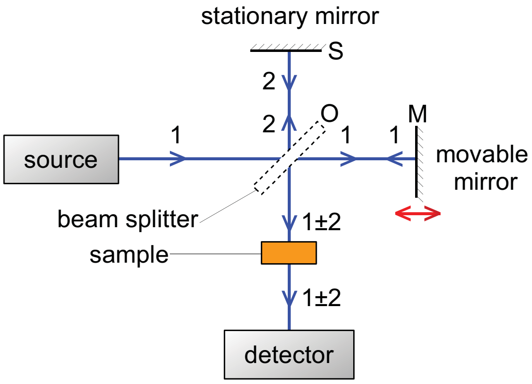


Figure 5.7: schematic Michelson interferometer.

In Fig. 5.7 there is interference, indicated as '1±2', between the two light beams reflected from the stationary mirror and the movable mirror. The interference depends upon the path difference, called the retardation δ (delta), between the two path from the beam splitter 'O' to and from the fixed mirror 'S' and the path from 'O' and to and from the movable mirror 'M'. The mirror 'M' is driven by a high precision digital electric motor so the retardation is accurately known. As a simple example of an interferogram Figs.5.8 shows the interferogram for a molecule with two zero-noise absorption peaks, one twice the intensity of the other at wavenumbers of 1 and 4 cm^{-1}.

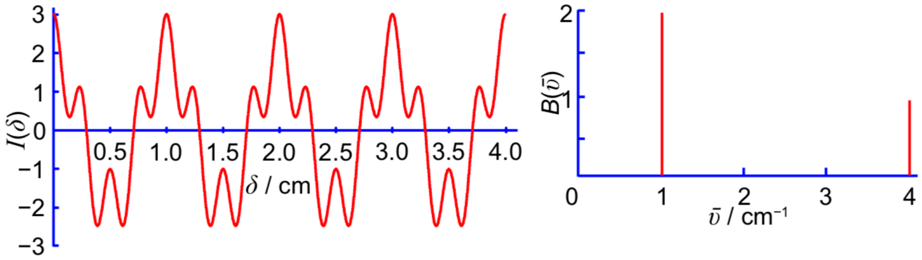
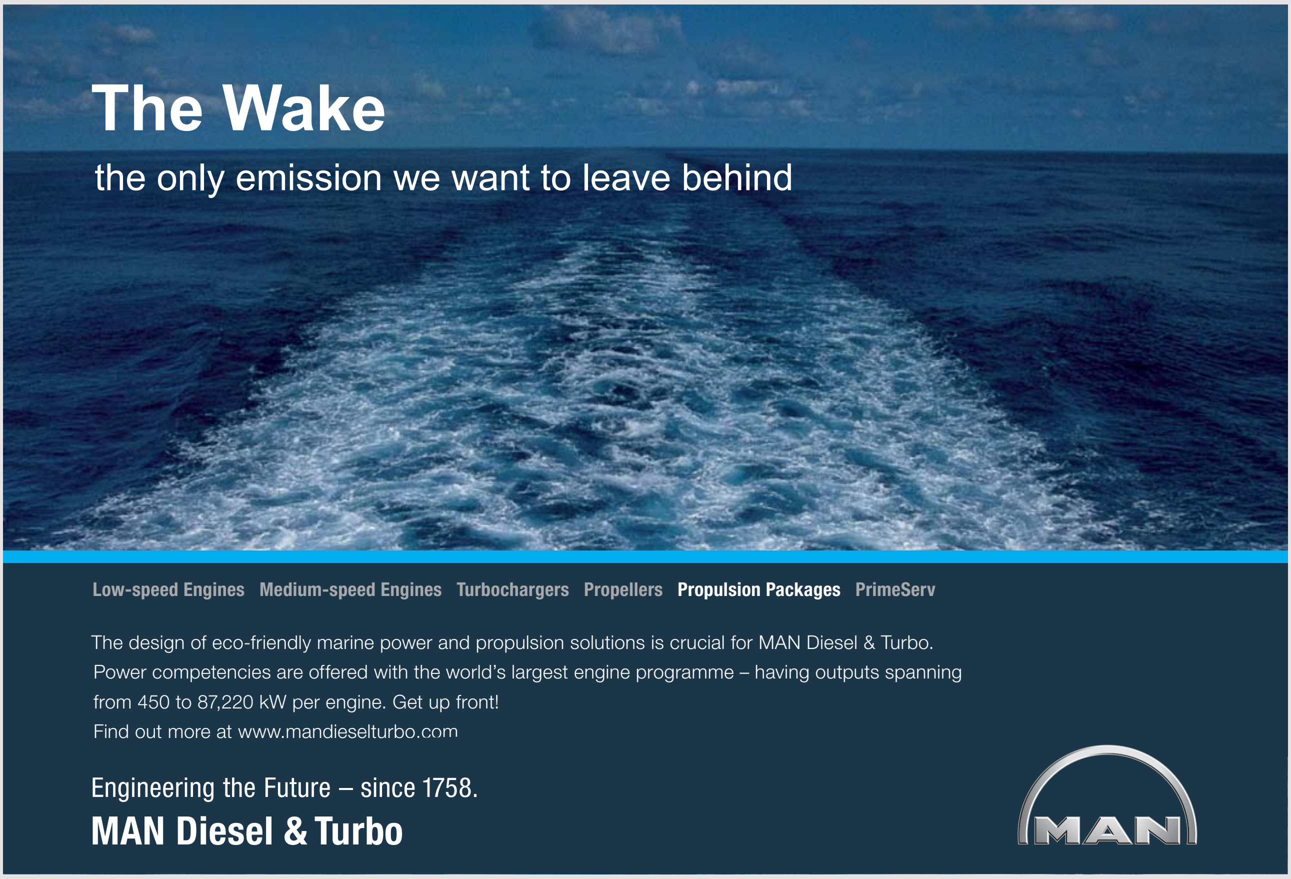


Figure 5.8: a simple interferogram signal (left) and transformed spectrum (right).



The interferogram is the intensity $I(\delta)$ as a function of the retardation $\delta = 2(\mathrm{OM} - \mathrm{OS})$. Using a Fourier transform the interferogram $I(\delta)$ is converted into the normal spectrum $B(\bar{\upsilon})$ in terms of wavenumber.

$$B(\bar{\upsilon}) = 2 \int_{\delta=0}^{\delta=\infty} I(\delta)\cos(2\pi\bar{\upsilon}\delta)\,\mathrm{d}\delta \quad \text{Fourier transform of an interferogram}$$

Clearly in a real spectrum there would be many peaks each with their own intensity, noise, and width so the interferogram $I(\delta)$ would be very complex.

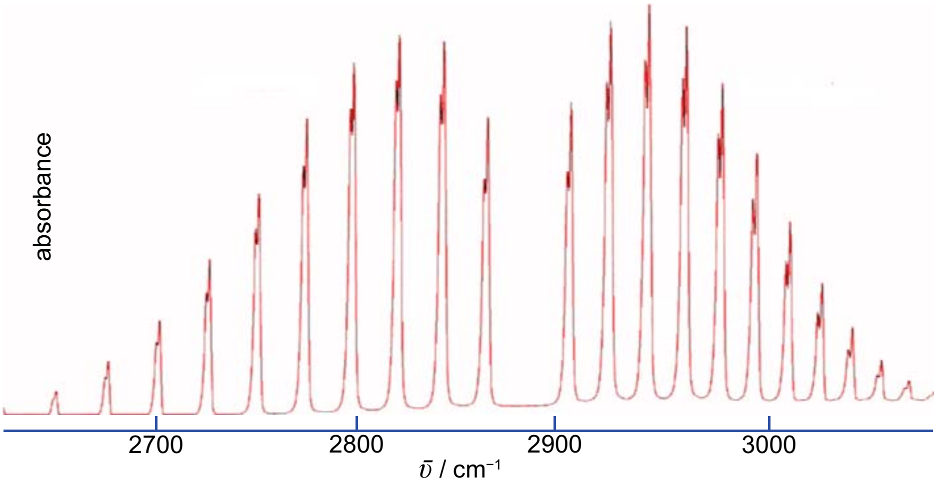


Figure 5.9: HCl gas infrared spectrum.

Fig. 5.9 is a teaching lab Fourier transform infrared spectrum of HCl gas where the peaks are due to transitions between various occupied rotational levels of the $v = 0$ vibrational level, to the $v = 1$ vibrational level in its accessible rotational levels (Parker 2015, chap 4). The peak splitting is due to the chlorine isotopes $H^{35}Cl$ and $H^{37}Cl$ with the larger of the pairs being due to $H^{35}Cl$.

Figure 5.10: HCl molecule.

An alternative method to using an interferometer commonly used in NMR and ion cyclotron resonance mass spectrometry 'ICR-MS' is a pulse of radiation and recording of the decay of the signal with time. The decaying signal is called a free induction decay FID $f(t)$. The normal spectrum is called a frequency domain spectrum $F(\omega)$. The angular frequency ω (omega) is the number of radians per second and is related to the normal frequency υ measured in Hertz or s^{-1} by $\omega = 2\pi\upsilon$. As it only takes a few seconds to obtain a FID one can add up many thousands of them to increase the signal to noise ratio. The frequency domain spectrum $F(\omega)$ is obtained from the time domain signal $f(t)$ by a Fourier transform and requires the solution of the integral below.

$$\overbrace{F(\omega)}^{\text{normal spectrum}} = \sqrt{\frac{2}{\pi}} \int_{t=0}^{t=\infty} \overbrace{f(t)}^{\text{time domain}} \cos(\omega t)\,\mathrm{d}t \qquad \text{Fourier transform of a free induction decay}$$

To understand the maths behind the Fourier transform process, let us take the simple example where an FID signal decays exponentially with time $f(t) = \exp(-at)$ where 'a' is the decay constant.

$$F(\omega) = \sqrt{\frac{2}{\pi}} \int_{t=0}^{t=\infty} \mathrm{e}^{-at} \cos(\omega t)\,\mathrm{d}t$$

For our example FID, find the frequency domain spectrum $F(\omega)$ using integration by parts, twice!

Jump to Solution 5 (see page 78)

5.1.6 QUESTION 6: INTEGRATED RATE LAW FOR A SECOND ORDER REACTION WITH TWO REACTANTS

For a reaction where two different reactants A and B react, and depending on the mechanism of reaction, the rate of reaction may be a function of the concentrations of both A and B molecules. In which case the reaction is called a second-order reaction.

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}$$

An important example in the stratosphere occurs in air that is polluted with chlorine containing molecules (both natural and man-made) which reacts with nitric oxide to form nitrosyl chloride.

$$\mathrm{NO} + \mathrm{Cl_2} \rightarrow \mathrm{NOCl} + \mathrm{Cl}$$

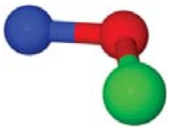


Figure 5.11: nitrosyl chloride.

$$v = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}] \qquad \text{Second-order rate law with two reactant species}$$

The starting concentrations of reactants at time $t = 0$ is $[A]_0$ mol L^{-1} and $[B]_0$ mol L^{-1} with no products C or D initially present. After a certain time t there will be x moles of C and x moles of D formed while x moles of A and B will have been consumed. To calculate the concentrations at a specific time we need to integrate the rate law above to get the 'integrated rate law'. We can then enter any specified time that we are interested in. We use the separation of variables and as the concentration at a time t are $[A] = ([A]_0 - x)$ and $[B] = ([B]_0 - x)$ then the integrated rate law is below.

$$\int_0^x \frac{1}{([A]_0 - x)([B]_0 - x)}\, dx = \int_0^t k\, dt$$

Calculate the integrated rate law using partial fractions (Parker 2018, section 1.3.8). Secondly, describe the graph you would plot to confirm whether this integrated equation is modelling our chemical reaction.

Jump to Solution 6 (see page 80)

5.2 WEEK 5 TUTORIAL SOLUTIONS

5.2.1 SOLUTION 1: DISSOLUTION OF A SOLID BY A SOLVENT

$$(1)\quad \int_{c=0}^{c=c} \frac{1}{c_s - c}\,\mathrm{d}c = \int_{t=0}^{t=t} k\,\mathrm{d}t \qquad (2)\quad \int_{z=c_s}^{z=c_s-c} \frac{1}{z}\,\mathrm{d}z = -k\int_{t=0}^{t=t} \mathrm{d}t$$

$$(3)\quad [\ln z]_{z=c_s}^{z=c_s-c} = -kt \qquad (4)\quad \ln\frac{c_s - c}{c_s} = -kt$$

$$(4)\quad \frac{c_s - c}{c_s} = \mathrm{e}^{-kt}$$

The integral (1) models a solid dissolving in a solvent. In (2) we substitute $z = c_s - c$ and $\mathrm{d}z = -\mathrm{d}c$ and take the negative to the right hand side and move the constant k outside the integral. We must also alter the limits of the integral in (2) to make them consistent with those of integral (1). The definite integral is (3). In (4) substitute back for z and take its antilog of both sides to give (5). Rearranging (5) gives the function modelling the dissolution process with time which is plotted in Fig. 5.12.

$$\frac{c}{c_s} = 1 - \mathrm{e}^{-kt}$$ Dissolution of a solid as a function of time

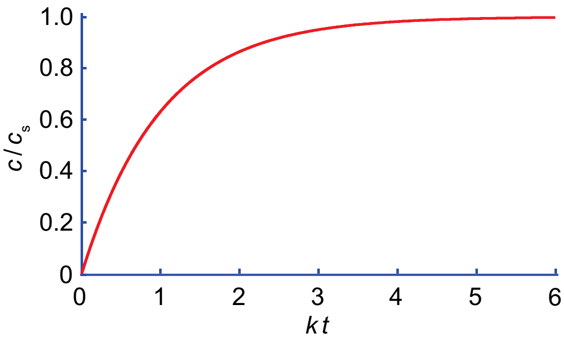


Figure 5.12: dissolution of a solid with time.

From Fig. 5.12 the dissolution of the solid molecule by the solvent is initially fast and then slows up logarithmically as the solution concentration approaches that of the saturated solution.

Return to Question 1 (see page 63)

5.2.2 SOLUTION 2: POPULATION OF DIATOMIC MOLECULES IN ROTATIONAL QUANTUM LEVELS

$$(1)\quad q_{\mathrm{r}} = \int_{J=0}^{J=\infty} (2J+1)\,\mathrm{e}^{-J(J+1)h^2/8\pi^2 I k_{\mathrm{B}} T}\,\mathrm{d}J$$

$$(2)\quad q_{\mathrm{r}} = \int_{z=0}^{z=\infty} \overset{\text{cancel}}{(2J+1)}\,\mathrm{e}^{-zh^2/8\pi^2 I k_{\mathrm{B}} T}\,\frac{\mathrm{d}z}{\underset{\text{cancel}}{2J+1}}$$

$$(3)\quad q_{\mathrm{r}} = \int_{z=0}^{z=\infty} \mathrm{e}^{-Az}\,\mathrm{d}z \qquad (4)\quad q_{\mathrm{r}} = \left[\frac{\mathrm{e}^{-Az}}{-A}\right]_{z=0}^{z=\infty} \qquad (5)\quad q_{\mathrm{r}} = \frac{1}{A}$$

In the rotational partition function (1) we substitute $z = J(J+1)$ which when written as $z = (J^2 + J)$ gives the derivative $\mathrm{d}z = (2J+1)\mathrm{d}J$ altering the limits appropriately in (2). The $(2J+1)$ terms cancel out in (2) and all the constants are $h^2/(8\pi^2 I k_{\mathrm{B}} T)$ are written as A in (3) for clarity. Integration of (3) gives (4) and the upper limit's exponential is zero and the lower limit leads to (5). The rotational partition function is just the reciprocal of A, the collection of constants for the given molecule at a given temperature.

$$q_{\mathrm{r}} = \frac{8\pi^2 I k_{\mathrm{B}} T}{h^2}$$ Rotational partition function of a diatomic molecule

Partition functions will be covered in your chemistry course later on, but now you know some of the maths involved in their manipulation.

Return to Question 2 (see page 64)

5.2.3 SOLUTION 3: CHEMISTRY AND RADIAL DISTRIBUTION FUNCTIONS

To calculate the average distance of an electron in a 1s atomic orbital of a H-atom we have to integrate the equation below using the integration of a product by the tabular method (Parker 2018, p 127).

$$<r_{1\mathrm{s}}> = \frac{4}{a_0^3}\int_{r=0}^{r=\infty} r^3\,\mathrm{e}^{-2r/a_0}\,\mathrm{d}r$$

We set up the table below with two rows. In row A each term is the differential of the preceding term and in row B each term is the integral of the preceding term.

A	$\mathrm{d}/\mathrm{d}r$	r^3	$3r^2$	$6r$	6	0
B	$\int \mathrm{d}r$	e^{-2r/a_0}	$\frac{-a_0}{2}\mathrm{e}^{-2r/a_0}$	$\frac{a_0^2}{4}\mathrm{e}^{-2r/a_0}$	$\frac{-a_0^3}{8}\mathrm{e}^{-2r/a_0}$	$\frac{a_0^4}{16}\mathrm{e}^{-2r/a_0}$

In the definite integral we multiply the first entry of row A (colour coded for clarity) with the second entry of row B; then the second entry of row A with the third entry of row B… alternating the signs starting with a positive sign and carry on until the product of the pairing is zero.

$$<r_{1s}> = \frac{4}{a_0^3}\left[+r^3\frac{-a_0}{2}e^{-2r/a_0} - 3r^2\frac{a_0^2}{4}e^{-2r/a_0} + 6r\frac{-a_0^3}{8}e^{-2r/a_0} - 6\frac{a_0^4}{16}e^{-2r/a_0}\right]_{r=0}^{r=\infty}$$

$$<r_{1s}> = \frac{4}{a_0^3}\frac{6a_0^4}{16}$$

When the upper limit is entered $e^{-\infty} = 0$, and all the upper limit terms are all zero. For the lower limit the exponential term $e^{-0} = 1$ and $r = 0$ so only the last term of the lower limit remains, that is $6a_0^4/16$ for the definite integral but remember the $4/a_0^3$ term outside the integral.

$$<r_{1s}> = \frac{3}{2}a_0 \quad \text{Average distance of a 1s electron in a H-atom}$$

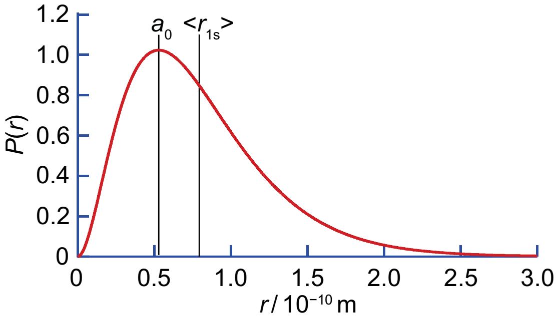


Figure 5.13: average distance of a 1s electron in a H-atom.

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Fig. 5.13 shows the average distance of the electron $<r_{1s}>$ = 0.7938 Å. However, there is an asymptotically small probability of the electron being at distances approaching infinity from the nucleus. Hence the conventional definition of an atomic or molecular orbital size is the contour surface enclosing 90% of the total probability.

Return to Question 3 (see page 49)

5.2.4 SOLUTION 4: COMPUTATIONAL CHEMISTRY

$$(1)\quad I_1 = \int_{r=0}^{r=\infty} r\,\mathrm{e}^{-ar^2}\,\mathrm{d}r \qquad (2)\quad z = ar^2 \quad \frac{\mathrm{d}z}{\mathrm{d}r} = 2ar \quad \frac{1}{2a}\mathrm{d}z = r\,\mathrm{d}r$$

$$(3)\quad I_1 = \frac{1}{2a}\int_{z=0}^{z=\infty} \mathrm{e}^{-z}\,\mathrm{d}z \qquad (4)\quad I_1 = \frac{1}{2a}\Big[-\,\mathrm{e}^{-z}\Big]_{z=0}^{z=\infty} \quad I_1 = \frac{1}{2a}$$

To integrate I_1 in (1) we substitute from (2) for $z = ar^2$ and $r\mathrm{d}r = \mathrm{d}z/2a_o$ to give (3) where the integration limits have been altered appropriately. The definite integral (4) the two limits are $\mathrm{e}^{-\infty} = 0$ and $\mathrm{e}^{-0} = 1$. The integral I_1 is equal to $I_1 = 1/2a$.

$$(5)\quad I_2 = \int_{r=0}^{r=\infty} r^2\,\mathrm{e}^{-ar^2}\,\mathrm{d}r \qquad (6)\quad I_2 = \int_{r=0}^{r=\infty} r\left(r\,\mathrm{e}^{-ar^2}\right)\mathrm{d}r$$

$$(6)\quad u = r \quad \mathrm{d}u = \mathrm{d}r \qquad (8)\quad \mathrm{d}v = r\,\mathrm{e}^{-ar^2}\,\mathrm{d}r \quad v = \int r\,\mathrm{e}^{-ar^2}\,\mathrm{d}r$$

To integrate I_2 (5) we will be using the integration by parts $\int u\mathrm{d}v = uv - \int v\mathrm{d}u$. In (6) we explicitly write r^2 as $r \times r$ in the pre-exponential term and then integrated by parts in (7) and (8).

$$(9)\quad t = r^2 \quad \frac{\mathrm{d}t}{\mathrm{d}r} = 2r \quad \frac{1}{2}\mathrm{d}t = r\,\mathrm{d}r$$

$$(10)\quad v = \int r\,\mathrm{e}^{-ar^2}\,\mathrm{d}r = \int \frac{1}{2}\mathrm{e}^{-at}\,\mathrm{d}t = \frac{-1}{2a}\,\mathrm{e}^{-at} = \frac{-1}{2a}\,\mathrm{e}^{-ar^2}$$

Before we can complete this first integration by parts in (8) we have to integrate the expression for v. We can do this by substituting $t = r^2$ and differentiating it as in (9) and then integrate in (10).

$$(11)\quad I_2 = \int_{r=0}^{r=\infty} r\left(r\,\mathrm{e}^{-ar^2}\right)\mathrm{d}r \qquad (12)\quad I_2 = \overbrace{\left[\frac{-r}{2a}\,\mathrm{e}^{-ar^2}\right]_{r=0}^{r=\infty}}^{uv} - \overbrace{\frac{-1}{2a}\int_{r=0}^{r=\infty} \mathrm{e}^{-ar^2}\,\mathrm{d}r}^{\int v\,\mathrm{d}u}$$

$$(13)\quad I_2 = \frac{1}{2a}\int_{r=0}^{r=\infty} \mathrm{e}^{-ar^2}\,\mathrm{d}r \qquad (14)\quad I_0 = \int_{r=0}^{r=\infty} \mathrm{e}^{-ar^2}\,\mathrm{d}r = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$(15)\quad I_2 = \frac{1}{4a}\sqrt{\frac{\pi}{a}}$$

The integration by parts in (6) may now be completed in (11) and (12) using the standard integral I_0 in (14) to give (15) the Gaussian integral I_2.

$$I_0 = \int_{r=0}^{r=\infty} \mathrm{e}^{-ar^2}\,\mathrm{d}r = \frac{1}{2}\sqrt{\frac{\pi}{a}} \qquad I_1 = \int_{r=0}^{r=\infty} r\,\mathrm{e}^{-ar^2}\,\mathrm{d}r = \frac{1}{2a}$$

$$I_2 = \int_{r=0}^{r=\infty} r^2\,\mathrm{e}^{-ar^2}\,\mathrm{d}r = \frac{1}{4a}\sqrt{\frac{\pi}{a}} \qquad I_3 = \int_{r=0}^{r=\infty} r^3\,\mathrm{e}^{-ar^2}\,\mathrm{d}r = \frac{1}{2a^2}$$

$$I_4 = \int_{r=0}^{r=\infty} r^4\,\mathrm{e}^{-ar^2}\,\mathrm{d}r = \frac{3}{8a^2}\sqrt{\frac{\pi}{a}} \qquad I_5 = \int_{r=0}^{r=\infty} r^5\,\mathrm{e}^{-ar^2}\,\mathrm{d}r = \frac{1}{a^3}$$

Including I_1 and I_2 that you have solved for yourself, I list the first few Gaussian integrals that are used in computational quantum chemistry, biology, biochemistry, and pharmaceutical chemistry. Note the differences between the even and odd Gaussian integrals.

Return to Question 4 (see page 69)

5.2.5 SOLUTION 5: SPECTROSCOPY AND FOURIER TRANSFORM

$$(1)\quad F(\omega) = \sqrt{\frac{2}{\pi}} \int_{t=0}^{t=\infty} \mathrm{e}^{-at}\cos(\omega t)\,\mathrm{d}t \qquad (2)\quad \frac{F(\omega)}{\sqrt{2/\pi}} = \int_{t=0}^{t=\infty} \mathrm{e}^{-at}\cos(\omega t)\,\mathrm{d}t$$

In the Fourier transform of our example FID signal (1) has for clarity the $\sqrt{(2/\pi)}$ term moved to the left hand side in (2). We are dealing with the integral of an exponential multiplied by a cosine function. We cannot use the tabular method of integration by parts as both the exponential and the cosine can be integrated or differentiated indefinitely.

We use integration by parts $\int u\,\mathrm{d}v = uv - \int v\,\mathrm{d}u$ twice. The reason we use it twice is the derivative of cosine is a minus-sine, and the derivative of minus-sine is minus-cosine, so we end with an expression closely related to the initial integral which can then be easily rearranged.

$$(3)\quad u = \cos(\omega t) \qquad (4)\quad \mathrm{d}u = -\omega\sin(\omega t)\,\mathrm{d}t$$

$$(4)\quad \mathrm{d}v = \mathrm{e}^{-at}\,\mathrm{d}t \qquad (6)\quad v = -\frac{1}{a}\mathrm{e}^{-at}$$

The u in (3) is differentiated to give $\mathrm{d}u$ (4) and $\mathrm{d}v$ in (5) is integrated to give v (6).

$$(7)\quad \frac{F(\omega)}{\sqrt{2/\pi}} = \left[\overbrace{(\cos(\omega t))}^{u}\overbrace{\left(-\frac{1}{a}\mathrm{e}^{-at}\right)}^{v}\right]_{t=0}^{t=\infty} - \int_{t=0}^{t=\infty}\overbrace{\left(-\frac{1}{a}\mathrm{e}^{-at}\right)}^{v}\overbrace{\left(-\omega\sin(\omega t)\,\mathrm{d}t\right)}^{\mathrm{d}u}$$

$$(8)\quad \frac{F(\omega)}{\sqrt{2/\pi}} = \frac{1}{a} - \frac{\omega}{a}\int_{t=0}^{t=\infty}\mathrm{e}^{-at}\sin(\omega t)\,\mathrm{d}t$$

The first integration by parts gives is (7). In the definite integral term in (7) in square brackets, the upper limit gives zero as $\mathrm{e}^{-\infty} = 0$ and the lower limit with $\mathrm{e}^{-0} = 1$ and $\cos(0) = 1$ the definite integral term equals $1/a$ as in (8). The intermediate result (8) leaves us with the problem of finding a solution to another integral by applying the second integration by parts $\int u\,\mathrm{d}v = uv - \int v\,\mathrm{d}u$.

$$(9)\quad u = \sin(\omega t) \qquad (10)\quad \mathrm{d}u = \omega\cos(\omega t)\,\mathrm{d}t$$

$$(11)\quad \mathrm{d}v = \mathrm{e}^{-at}\,\mathrm{d}t \qquad (12)\quad v = -\frac{1}{a}\mathrm{e}^{-at}$$

This second integration by parts has u as a sine function (9) whose derivative is (10) and $\mathrm{d}v$ is again the exponential in (11) whose integral is (12).

$$(13)\quad \frac{F(\omega)}{\sqrt{2/\pi}} = \frac{1}{a} - \frac{\omega}{a}\left(\left[\overbrace{(\sin(\omega t))}^{u}\overbrace{\left(\frac{-1}{a}\mathrm{e}^{-at}\right)}^{v}\right]_{t=0}^{t=\infty} - \int\limits_{t=0}^{t=\infty}\overbrace{\frac{-1}{a}\mathrm{e}^{-at}}^{v}\,\overbrace{\omega\cos(\omega t)\,\mathrm{d}t}^{\mathrm{d}u}\right)$$

$$(14)\quad \frac{F(\omega)}{\sqrt{2/\pi}} = \frac{1}{a} - \frac{\omega^2}{a^2}\int\limits_{t=0}^{t=\infty}\mathrm{e}^{-at}\cos(\omega t)\,\mathrm{d}t \;=\; \frac{1}{a} - \frac{\omega^2}{a^2}\frac{F(\omega)}{\sqrt{2/\pi}}$$

$$(15)\quad \left(1 + \frac{\omega^2}{a^2}\right)\frac{F(\omega)}{\sqrt{2/\pi}} = \frac{1}{a}$$

$$(16)\quad \frac{F(\omega)}{\sqrt{2/\pi}} = \frac{a}{a^2 + \omega^2}$$

The sine function in the intermediate result (8) is integrated using the second integration by parts to give (13). For the definite integral of (13) in square brackets the upper limit is zero as $\mathrm{e}^{-\infty} = 0$ and the lower limit is also zero as $\sin(0) = 0$. So (13) becomes (14). The integral term in (14) is equal to the transformed signal divided by the square root of two over pi. Equation (14) is rearranged to (15) and then (16).

The Fourier transform of our simple exponential time domain decay function (2), not forgetting the $\sqrt{(2/\pi)}$ factor, is given by the simple equation below.

$$F(\omega) = \sqrt{\frac{2}{\pi}}\,\frac{a}{a^2+\omega^2} \qquad \text{FT of the time domain signal } \exp(-at)$$

Return to Question 5 (see page 69)

5.2.6 SOLUTION 6: INTEGRATED RATE LAW FOR A SECOND ORDER REACTION WITH TWO REACTANTS

$$(1)\quad \int\limits_{0}^{x}\frac{1}{([\mathrm{A}]_0-x)([\mathrm{B}]_0-x)}\,\mathrm{d}x = kt$$

$$(2)\quad \frac{1}{([\mathrm{A}]_0-x)([\mathrm{B}]_0-x)} \equiv \frac{A}{([\mathrm{A}]_0-x)} + \frac{B}{([\mathrm{B}]_0-x)}$$

$$(3)\quad \frac{1}{([\mathrm{A}]_0-x)([\mathrm{B}]_0-x)} \equiv \frac{A([\mathrm{B}]_0-x) + B([\mathrm{A}]_0-x)}{([\mathrm{A}]_0-x)([\mathrm{B}]_0-x)}$$

In order to be able to integrate the rate law (1) we need to change the fraction on the left into a sum of two separate fractions. We use 'partial fractions' (Parker 2018, p 32) before we can integrate the equation. We write in (2) the 'identity function' for the partial fraction. Firstly, don't confuse the variables *A* and *B* (in italics and as yet unknown quantities) and the chemical labels A and B (in roman type). Secondly, the identity '≡' is true for *all* values of x whereas an equation '=' is only true for certain values of x, these are the solutions or the roots of the equation. Bringing the two terms on the right of the identity (2) to a common denominator gives (3). In (3) the two numerator are identical to each other as well as the two denominators being identical to each other.

$$(4)\quad 1 \equiv A\left([\mathrm{B}]_0 - [\mathrm{A}]_0\right) \qquad (5)\quad A \equiv \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}$$

$$(6)\quad 1 \equiv B\left([\mathrm{A}]_0 - [\mathrm{B}]_0\right) \qquad (7)\quad B \equiv \frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0}$$

$$(7)\quad \frac{1}{\left([\mathrm{A}]_0 - x\right)\left([\mathrm{B}]_0 - x\right)} \equiv \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\left(\frac{1}{[\mathrm{A}]_0 - x} - \frac{1}{[\mathrm{B}]_0 - x}\right)$$

To find the value of A we know that the identity is true for $x = [\mathrm{A}]_0$ which makes the numerators in (3) equal to (4) and so unknown multiplier A is equal to (5). The identity is also true for $x = [\mathrm{B}]_0$ which makes the numerators in (3) identical to (6) and the other unknown multiplier is B identical to (7), note that $A = -B$. Substitute these derived values for the variables A and B into (2) and take out the common factor $([\mathrm{B}]_0 - [\mathrm{A}]_0)$ outside brackets gives (8). The partial fraction (8) allow us to now evaluate the integral for our second-order chemical kinetics equation (1).

$$(8)\quad \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0} \int_0^x \left(\frac{1}{[\mathrm{A}]_0 - x} - \frac{1}{[\mathrm{B}]_0 - x}\right) \mathrm{d}x = k\,t$$

$$(10)\quad \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0} \Big[-\ln\left([\mathrm{A}]_0 - x\right) + \ln\left([\mathrm{B}]_0 - x\right) \Big]_0^x = k\,t$$

$$(11)\quad \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0} \quad \overbrace{-\ln\left([\mathrm{A}]_0 - x\right) + \ln\left([\mathrm{B}]_0 - x\right)}^{\text{upper limit}} \overbrace{+ \ln[\mathrm{A}]_0 - \ln[\mathrm{B}]_0}^{\text{minus lower limit}} = k\,t$$

The definite integral (9) gives the log terms in (10) which entering the two limits gives us (11). From the rules of logs (Parker 2018, section 3.1.2) we can replace the subtraction of two logs by the log of the ratio and also we take the common factor which was outside the integral over to the right to get the integrated second-order rate law for two reactants.

$$\ln \frac{[\mathrm{A}]_0 \left([\mathrm{B}]_0 - x\right)}{[\mathrm{B}]_0 \left([\mathrm{A}]_0 - x\right)} = k\left([\mathrm{B}]_0 - [\mathrm{A}]_0\right) t \qquad \text{Integrated second-order rate law for two reactants}$$

Evidence in support that our chemical reaction is modelled as an integrated second-order rate law comes from the plot shown in Fig. 5.14 where a straight line graph is supporting evidence and the gradient allows the rate constant k to be measured. Note we have to measure [A] and or [B] as a function of time by accurate chemical analysis to find x.

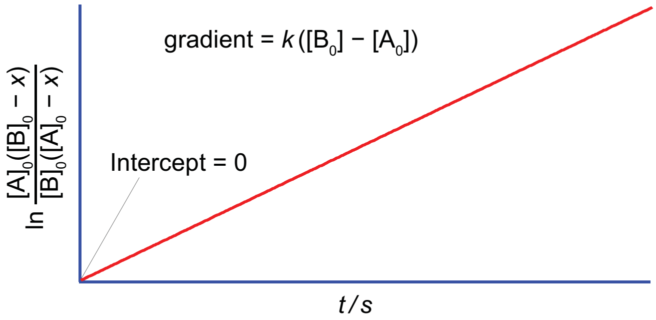


Figure 5.14: integrated rate law plot for a second-order reaction with two reactants.

Return to Question 6 (see page 72)

6 WEEK 6 CHEMICAL APPLICATIONS OF INTEGRATION

This week's tutorials cover four topics: (1) area under a curve, (2) average value of a function, (3) the length of curves, and (4) the trapezium rule. All of these find applications in different areas of chemistry.

6.1 WEEK 6 TUTORIAL QUESTIONS

6.1.1 QUESTION 1: ENTROPY MEASUREMENT OF SOLID BISMUTH

How do we measure the entropy of a substance? It is relatively 'easy' to measure the amount of heat required to raise the temperature of one mole of material by one kelvin (or one degree Celsius). If this is measured at a constant pressure (for instance, one atmosphere) then it is called the heat capacity at constant pressure C_p and repeating these measurements at a series of temperatures then we can convert from heat capacity to entropy. Bismuth is a metal which expands on freezing and for this reason is used in printers' type, it is also used in medicine, as an alloy for thermocouples, as a nuclear reactor carrier for uranium, and in cosmetics. Bismuth's heat capacity slowly increases with temperature.

C_p° / J K^{-1} mol^{-1}	23	23.74	24.25	24.44	24.61	24.89	25.11
T / K	100	120	140	150	160	180	200

The change in entropy of a substance due to changing its temperature is given by the area under the curve of a graph of heat capacity at constant pressure divided by temperature, plotted against T (the integral of the curve between the two temperatures). Fig. 6.1 shows the plot of the above data.

$$\Delta S(T_2 - T_1) = \int_{T_1}^{T_2} \frac{C_p}{T}\,\mathrm{d}T \qquad \text{Entropy from heat capacity and temperature data}$$

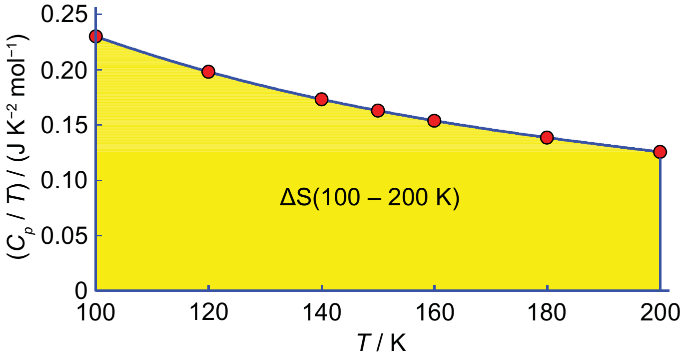


Figure 6.1: C_p / T versus T for bismuth metal.

Fig.6.1 shows that the data is 'smooth' and of high quality and we may fit a polynomial to the data. The spreadsheet best fit to the data is a third-order polynomial from 100 K to 200 K but we must not extrapolate outside this range.

$$\frac{C_p}{T} = a_0 + a_1 T + a_2 T^2 + a_3 T^3$$

Integrate the polynomial. Then enter the values for the coefficients (for clarity the units are not included) to find the entropy change for bismuth in heating the metal from 100 K to 200 K at a constant pressure.

a_0	a_1	a_2	a_3
$+0.5505$	-4.932×10^{-3}	$+2.050\times10^{-5}$	-3.229×10^{-8}

Jump to Solution 1 (see page 90)

6.1.2 QUESTION 2: ELECTRON PROBABILITIES IN A GROUND STATE HYDROGEN ATOM

I am summarizing the introduction to question 5.1.3 here to help clarify the concepts.

wavefunction

$$(1)\quad \psi_{1s} = \sqrt{\frac{1}{\pi a_0^3}}\ \mathrm{e}^{-r/a_0}$$

probability density

$$(2)\quad {\psi_{1s}}^2 = \frac{1}{\pi a_0^3}\ \mathrm{e}^{-2r/a_0}$$

$$(3)\quad P_{1s}(r) = \frac{4}{a_0^3} r^2\, \mathrm{e}^{-2r/a_0}$$

radial distribution function

$$(4)\quad P_{1s}(r_1\text{-}r_2) = \frac{4}{a_0^3}\int_{r_1}^{r_2} r^2\, \mathrm{e}^{-2r/a_0}\, \mathrm{d}r$$

probability between r_1 and r_2

The wavefunction ψ_{1s} of an electron in the 1s orbital of a hydrogen atom is (1) where a_0 is the Bohr radius 0.5292 Å and r is the distance of the electron from the nucleus. The probability that the electron is in a small cubic volume of space $\mathrm{d}\tau$ from the nucleus is equal to the square of the wavefunction multiplied by the small volume ${\psi_{1s}}^2\mathrm{d}\tau$. If we divide by the small volume $\mathrm{d}\tau$ we obtain (2) the probability density per unit volume which is known as the 'probability density' ψ_{1s}^2 note the $2r$ term in the exponential from squaring the wavefunctions. Fig. 6.2, the probability density has a non-zero value at the nucleus of $1/\pi a_0^3$ which is 2.1478 Å^3 because all the probability density is crammed into a small volume around the nucleus where the 1s wavefunction is a maximum. So perhaps the concept of probability density is not very 'meaningful', however, there is a more intuitive approach.

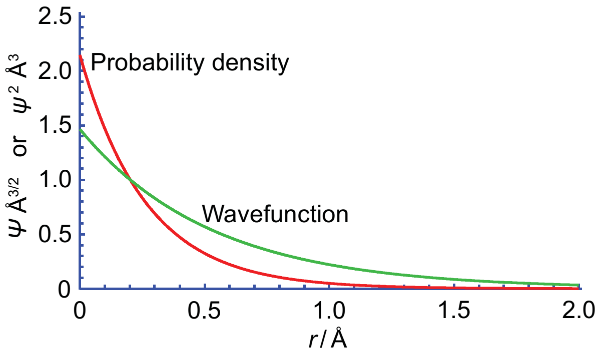


Figure 6.2: H-atom 1s-electron wavefunction and probability density.

(3) Perhaps of greater interest is the probability of the electron being in a thin spherical shell between two concentric spheres which are at a distance from the nucleus of r and (r+dr).

$$V(r+\mathrm{d}r)-V(r)=\frac{4}{3}\pi\left(r^3+3r^2\,\mathrm{d}r+\overbrace{3r(\mathrm{d}r)^2+(\mathrm{d}r)^3}^{\text{negligible}}-r^3\right)=4\pi r^2\,\mathrm{d}r$$

The $4\pi r^3/3$ terms, in red, cancel. The terms involving powers of the infinitesimal distance dr are negligible and can be ignored. The volume of the thin shell is $4\pi r^2\mathrm{d}r$ and the probability of the electron being in this shell $4\pi r^2\psi_{1s}{}^2\mathrm{d}r$. If we divide by d$r$ we obtain the probability density per unit distance known as the 'radial distribution function' $P(r)$.

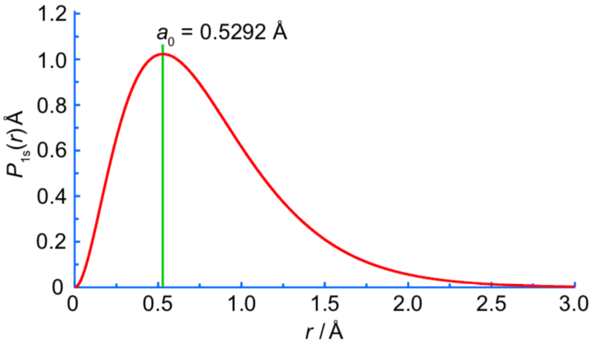


Figure 6.3: H-atom 1s-electron radial distribution function.

Fig. 6.3 shows that the H-atom 1s radial distribution function which is skewed towards high values of the radius due to the r-squared term, this term also makes the radial distribution function zero at the nucleus. The most probable distance for electron is at the maximum called the Bohr radius a_0 which is at 0.5292 Å.

(4) The probability of the 1s H-atom electron being located between radii r_1 and r_2 from the nucleus is the integral (area under the curve) of radial distribution function between these limits.

Calculate the probabilities of the hydrogen ground state electron being between the following distances from the nucleus: (a) $P(0\text{-}a_0)$, (b) $P(0\text{-}\infty)$, and (c) calculate the radius of the 1s atomic orbital of the H-atom using the conventional 90% probability definition for atom and molecular orbitals. These integrations are best done by the integration by parts using the tabular method (Parker 2018, section 8.1.3). Comment on your results!

Jump to Solution 2 (see page 90)

6.1.3 QUESTION 3: THE AVERAGE KINETIC ENERGY OF GAS MOLECULES

$$f(c_x)=\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{1/2}\mathrm{e}^{-mc_x^2/2k_\mathrm{B}T}$$

$$f(c_x)=\left(\frac{M}{2\pi RT}\right)^{1/2}\mathrm{e}^{-Mc_x^2/2RT}$$

Maxwell-Boltzmann distribution in one-dimension

In the kinetic theory of gases, the probability that a molecule of mass *m* kilograms (or molar mass *M* kg mol^{-1}) at temperature *T* will have a speed (not velocity) in the *x* direction between c_x and $c_x + \mathrm{d}c_x$ is given by the Maxwell-Boltzmann speed distribution in one-dimension. Where k_B is Boltzmann's constant and *R* is the gas constant.

$$(1)\quad <T_x> = \int_{c_x=-\infty}^{c_x=+\infty} \frac{1}{2} m c_x^2 \left(\frac{m}{2\pi k_B T}\right)^{1/2} \mathrm{e}^{-m c_x^2/2k_B T}\, \mathrm{d}c_x$$

$$(2)\quad u = \left(\frac{m}{2k_B T}\right)^{1/2} c_x \qquad (3)\quad \int_{x=-\infty}^{x=+\infty} x^2\, \mathrm{e}^{-x^2}\, \mathrm{d}x = \frac{1}{2}\sqrt{\pi}$$

(1) The average kinetic energy in the *x* direction $<T_x>$ is obtained by evaluating the integral of the product of $\frac{1}{2} m c_x^2$ and $f(c_x)$ between the limits of plus and minus infinite speed. Obtain an expression for the average kinetic energy of gas molecules in the *x* direction by solving (1). I suggest you make use of the substitution (2) and the standard integral (3).

Jump to Solution 3 (see page 96)

6.1.4 QUESTION 4: TRAPEZIUM RULE INTEGRATION OF HEAT CAPACITY DATA TO CALCULATE ENTROPY

Obtaining thermodynamic functions, such as the entropy, from experimental measurements often requires numerical integration of a function. One way to do this consists in remembering that the definite integral is the area under the curve and applying the trapezium rule. Alternatively, data can be fitted to a function and then integrated. Question 4 uses the trapezium rule and question 5 fits a function to the same data. We may then compare the two methods.

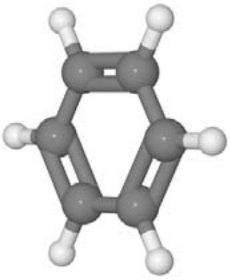


Figure 6.4: benzene, dark grey C, grey H.

Benzene freezes below 5.5 °C. Shown below are a students experimental heat capacity data for solid benzene (using appropriate safety measures) at several temperatures up to 273 K (Fig. 6.5 to three decimal places).

	A	B	C	D	E	F	G	H
1	T / K	23.000	48.000	73.000	123.000	173.000	223.000	273.000
2	C(p) / (J / K / mol)	13.010	29.660	40.460	55.440	74.060	97.610	122.300

Figure 6.5: spreadsheet data for trapezium rule integration.

First, before we carry out the numerical integration of the data from 23 K to 273 K we must integrate from 0 to 23 K. The heat capacity at temperatures approaching zero kelvin is accurately given by the Debye *T*-cubed law where '*a*' is a constant. So we can use the heat capacity at 23 K to find the value of '*a*'.

$$C_p = aT^3 \quad \text{Debye } T\text{-cubed law for temperatures near zero kelvin}$$

Secondly, from the graph of C_p/T against T apply the trapezium rule to numerically integrate from 23 to 273 K using the relationship between heat capacity divided by temperature.

$$\Delta S(23-273\,\mathrm{K}) = \int_{T=23}^{T=273} \frac{C_p}{T}\,\mathrm{d}T$$

Thirdly, the total entropy *S*(273 K) of solid benzene at 273 K is the sum of the two contributions 0-23 K and 23-273 K.

Jump to Solution 4 (see page 96)

6.1.5 QUESTION 5: POLYNOMIAL INTEGRATION FOR THE ENTROPY OF BENZENE FROM HEAT CAPACITY DATA

In question 4 we used the trapezium rule which treats the C_p/T as a non-continuous function of T with only 7 data point between 23 and 273 K. When a large number of data points have been measured the trapezium rule is easy and fast to apply using a spreadsheet. Alternatively we may treat our C_p data as a continuous function of T by fitting a polynomial function to the C_p versus T graph. We then substitute the polynomial for C_p into the integral equation below and then integrate the polynomial of C_p where each term is divided by T.

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T}\,\mathrm{d}T$$

First, plot the heat capacity data of solid benzene reported in question 4 against temperature using a spreadsheet.

Secondly, fit a polynomial to the curve using both the goodness of fit parameter R as well as your judgement to find the best order of the polynomial. A polynomial is very useful as it fits the data over a given range (23 K to 273 K in this case) but it does not give us any new chemical insight. However, polynomial functions are easy to integrate (or differentiate). But what we cannot do is to extrapolate the polynomial function outside the limits of where it gives agreement with the experimental data. This is because it is not a 'model' based equation, it is only a useful numerical fit.

Thirdly, integrate and find the change in entropy, ΔS(23-273 K) when solid benzene is heated from 23 to 273 K. Use your previous value for ΔS(0-23 K) from the Debye T-cubed law (section 6.2.4) to find the entropy of solid benzene at 273 K. Comment on the comparison of the numerical and analytical integration of data.

Jump to Solution 5 (see page 99)

6.2 WEEK 6 TUTORIAL SOLUTIONS

6.2.1 SOLUTION 1: ENTROPY MEASUREMENT OF SOLID BISMUTH

Integrating the polynomial fit to the data $(C_p/T) = a_0 + a_1T + a_2T^2 + a_3T^3$ we calculate the entropy change for bismuth on heating from 100 K to 200 K. For clarity I will ignore the units of the coefficients.

$$\text{(1)}\quad \Delta S(100\text{-}200\,\mathrm{K}) = \left[a_0T + a_1T^2/2 + a_2T^3/3 + a_3T^4/4\right]_{T=100}^{T=200}$$

$$\begin{aligned}\text{(2)}\quad \Delta S(100\text{-}200\,\mathrm{K}) &= 0.5505\times(200-100) - (4.932\times10^{-3})(200^2-100^2)/2\\ &+ (2.050\times10^{-5})(200^3-100^3)/3 - (3.229\times10^{-8})(200^4-100^4)/4\end{aligned}$$

$$\text{(3)}\quad \Delta S(100\text{-}200\,\mathrm{K}) = 55.05 - 73.98 + 47.83 - 12.11 = 16.79$$

A place where errors may creep in is in step (2) when entering the limits. Some people might say the temperature difference is 100 K and incorrectly try to take powers of 100. The entropy change of bismuth metal on heating from 100 K to 200 K is 16.79 J K^{-1} mol^{-1}.

Return to Question 1 (see page 83)

6.2.2 SOLUTION 2: ELECTRON PROBABILITIES IN A GROUND STATE HYDROGEN ATOM

The probability integral below is the product of two terms involving the distance from the nucleus r^2 and $\exp(-2r/a_0)$. Set up the table for the integration by parts with two rows. In row (A) starting with r^2 each term is the differential of the preceding term and in row (B) starting with $\exp(-2r/a_0)$ each term is the integral of the preceding term.

$$P(r) = \frac{4}{a_0^3}\int_{r=0}^{r=r} r^2\,\mathrm{e}^{-2r/a_0}\,\mathrm{d}r$$

$$\begin{array}{lllllll}
\text{(A)} & \mathrm{d}/\mathrm{d}r & & \boldsymbol{r^2} & \boldsymbol{2r} & \boldsymbol{2} & 0\\
\text{(B)} & \int \mathrm{d}r & \mathrm{e}^{-2r/a_0} & \boldsymbol{\frac{-a_0}{2}\mathrm{e}^{-2r/a_0}} & \boldsymbol{\frac{a_0^2}{4}\mathrm{e}^{-2r/a_0}} & \boldsymbol{\frac{-a_0^3}{8}\mathrm{e}^{-2r/a_0}} &
\end{array}$$

For clarity the entries in the table are colour coded, we pair the first entry of row (A) with the second entry of row (B), then the second entry of row (A) with the third entry of row (B)… alternating the signs starting with a positive sign and carry on until the product of the pairing is zero.

$$(1)\quad P(r) = \frac{4}{a_0^3}\left[(+)r^2\frac{-a_0}{2}\mathrm{e}^{-2r/a_0}\ (-)2r\frac{a_0^2}{4}\mathrm{e}^{-2r/a_0}\ (+)2\frac{-a_0^3}{8}\mathrm{e}^{-2r/a_0}\right]_{r=0}^{r=r}$$

$$(2)\quad P(r) = \frac{4}{a_0^3}\left[-\frac{a_0 r^2}{2}\mathrm{e}^{-2r/a_0} - \frac{a_0^2 r}{2}\mathrm{e}^{-2r/a_0} - \frac{a_0^3}{4}\mathrm{e}^{-2r/a_0}\right]_{r=0}^{r=r}$$

In (1) the alternating signs are shown in brackets for clarity and we must also remember the $4/a_o{}^3$ term outside the probability integral. The integral (1) is tidied up in (2).

$$(3)\quad P(0\text{-}a_0) = \frac{4}{a_0^3}\left[-\frac{a_0 r^2}{2}\mathrm{e}^{-2r/a_0} - \frac{a_0^2 r}{2}\mathrm{e}^{-2r/a_0} - \frac{a_0^3}{4}\mathrm{e}^{-2r/a_0}\right]_{r=0}^{r=a_0}$$

$$(4)\quad P(0\text{-}a_0) = \frac{4}{a_0^3}\left[\left(-\frac{a_0^3}{2}\mathrm{e}^{-2} - \frac{a_0^3}{2}\mathrm{e}^{-2} - \frac{a_0^3}{4}\mathrm{e}^{-2}\right) - \left(-0 - 0 - \frac{a_0^3}{4}\right)\right]$$

$$(5)\quad P(0\text{-}a_0) = \frac{4}{a_0^3}\left[-\frac{5a_0^3}{4}\mathrm{e}^{-2} + \frac{a_0^3}{4}\right] = -5\mathrm{e}^{-2} + 1 = 0.3233$$

(a) For the probability from $r = 0$ to $r = a_0$ the integral (2) becomes (3). We are dealing with negative exponential functions, see Fig. 6.6. Entering the upper limit $r = a_0$ and the lower limit $r = 0$ with $\exp(-0) = 1$ leads to (4) and (5).

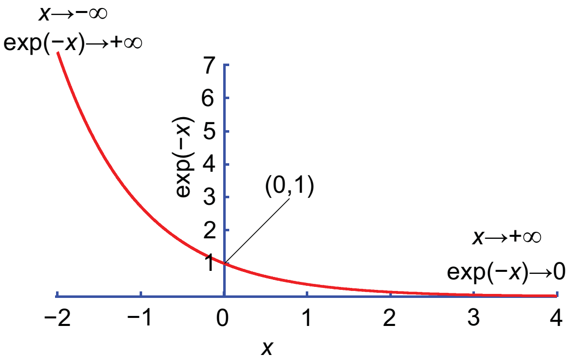


Figure 6.6: negative exponential function.

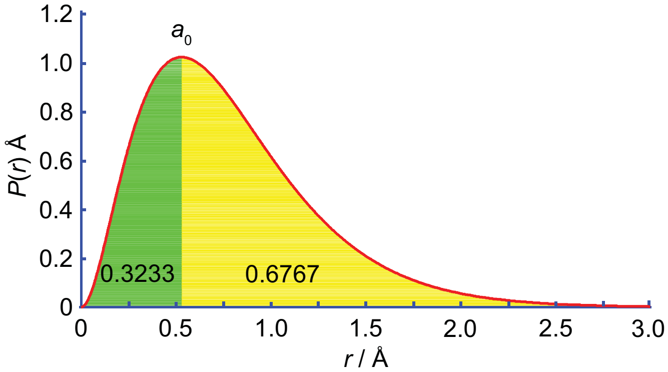


Figure 6.7: 1s H-atom radial distribution function and $P(0\text{-}a_0)$.

(a) The Bohr theory of the H-atom had the electron circulating at a fixed distance of 0.5292 Å, the Bohr radius. The wave mechanics interpretation of quantum theory means we can only measure probabilities and although the most probable distance is the Bohr radius the electron only spends about 32% of its time between the nucleus and the Bohr radius, the area under the curve (green) in Fig.6.7 and about 68% of its time between the Bohr radius and infinity (yellow). This is because there is zero probability of the electron being at the nucleus and small probabilities of it being close to the nucleus. That is the probability distribution function is skewed towards large distances with a sharp rise up to the maximum and a slow fall-off to larger distances, hence a smaller area to the left compared to the right of the maximum. The most probable distance for the 1s H-atom electron is the maximum of the probability distribution function.

(b) To calculate the probability from $r = 0$ to $r = \infty$ the upper limit $r = \infty$ in (6) makes the exponentials $\exp(-\infty) = 0$, see Fig. 6.6 for a negative exponential. The lower limit $r = 0$ makes all the terms equal to zero that have r in the pre-exponential, leaving only the term with no r in the exponential as $\exp(0)$ is equal to one.

$$(6)\quad P(0-\infty)=\frac{4}{a_0^3}\left[-\frac{a_0 r^2}{2}e^{-2r/a_0}-\frac{a_0^2 r}{2}e^{-2r/a_0}-\frac{a_0^3}{4}e^{-2r/a_0}\right]_{r=0}^{r=\infty}$$

$$(7)\quad P(0-\infty)=\frac{4}{a_0^3}\left[(-0-0-0)-\left(-0-0-\frac{a_0^3}{4}\right)\right]=1$$

In (7) we have the probability $P(0\text{-}\infty) = 1$ this is because the 1s H-atom wavefunction we are using is 'normalized' with the normalization factor $(1/\pi a_0^3)^{1/2}$. You have just proved for yourself that the wavefunction used to calculation the probability function in Fig. 6.8 is normalized (Parker 2018, p 131).

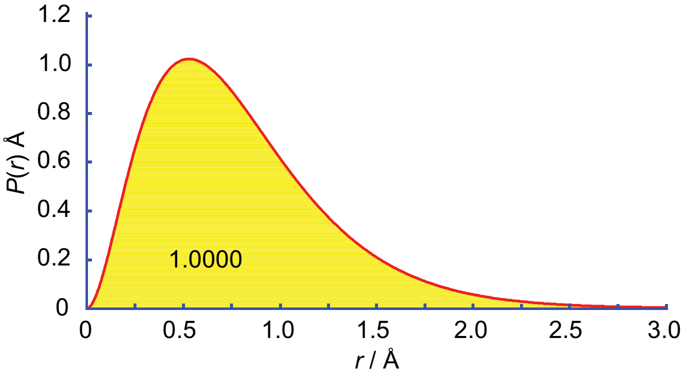


Figure 6.8: total radial probability for a normalized 1s H-atom wavefunction.

So the electron could be at an infinite distance from its nucleus but with negligible probability of this happening. So how can we talk about the size of an atomic or a molecular orbital? The accepted definition is to draw a contour surface which encloses a constant and large probability (usually 90%) of the total probability. What is the distance for the contour surface for the 1s atom orbital, this is answered in part (c) below.

(c) To find the radius of the 1s atomic orbital for the H-atom we take integral (2) and set the total probability to 0.9 (90%) and we need to find the upper limit distance r_{1s} in (8).

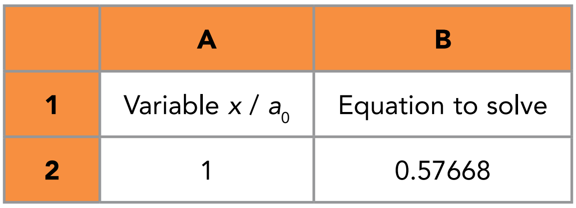
$$(8)\quad 0.9=\frac{4}{a_0^3}\left[-\frac{a_0 r^2}{2}e^{-2r/a_0}-\frac{a_0^2 r}{2}e^{-2r/a_0}-\frac{a_0^3}{4}e^{-2r/a_0}\right]_{r=0}^{r=r_{1s}}$$

$$(9)\quad 0.9=\frac{4}{a_0^3}\left(-\frac{a_0 r_{1s}^2}{2}e^{-2r_{1s}/a_0}-\frac{a_0^2 r_{1s}}{2}e^{-2r_{1s}/a_0}-\frac{a_0^3}{4}e^{-2r_{1s}/a_0}+\frac{a_0^3}{4}\right)$$

$$(10)\quad 0.9=\frac{4}{a_0^3}\left(-\frac{x^2 a_0^3}{2}e^{-2x}-\frac{x a_0^3}{2}e^{-2x}-\frac{a_0^3}{4}e^{-2x}+\frac{a_0^3}{4}\right)$$

$$(11)\quad e^{-2x}(2x^2+2x+1)-0.1=0$$

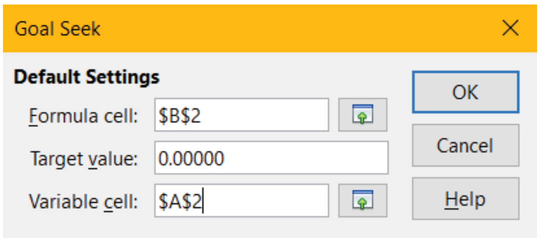
Entering the limits in (8) gives us (9). To solve (9) for r_{1s} we make the substitution $x = r_{1s}/a_0$ that is we are expressing the distance in bohrs in (10). In (11) we multiply by minus throughout, the 0.9 is taken over to the right, and the common factor $\exp(-2x)$ is taken out of the brackets.



	A	B
1	Variable x / a_0	Equation to solve
2	1	0.57668

Figure 6.9: spreadsheet entries for solving equation (11).

In Fig.6.9 cells A1 and B1 are just the names of the data entries so we know what we are doing. A2 is the initial guess of 1 for the variable x. B2 enter the equation =EXP(-2*A2)*(2*A2^2+2*A2+1)-0.1 for solving (11) for x. Once we have entered the equation in B2 and pressed 'return' then the cell B2 displays 0.57668 to 5 significant figures. Clearly the equation is not equal to zero with the initial guess of $x = 1$. With the cursor on B2 click on 'Tools' then 'Goal seek' in *Calc* (Libre Office, 2018) and a dialogue box opens, Fig. 6.10.



Goal Seek

Default Settings

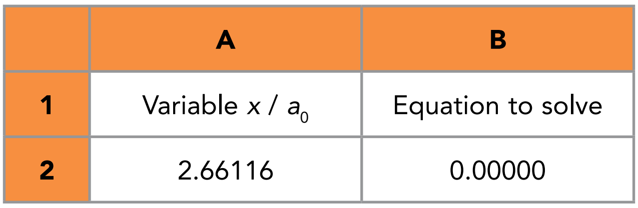
Formula cell: B2

Target value: 0.00000

Variable cell: A2

Figure 6.10: goal seek dialogue box.

The 'Formula cell' is automatically entered as B2. In the 'Target value' window type in 0.00000 as we want to find the roots of the equation to at least six significant figures. Finally in the 'Variable cell' window type in A2 which at the moment contains the initial guess of unity. Clicking OK and the spreadsheet solves the equation and asks if you want the result entered into the variable cell A2, click OK, and we get the root of the equation, Fig. 6.11.



	A	B
1	Variable x / a_0	Equation to solve
2	2.66116	0.00000

Figure 6.11: final spreadsheet after goal seeking the root of the equation.

The solution in A2 is x = 2.66116 bohr. Hence the 90% atomic orbital radius in angstroms is equal to r_{1s} = (2.66116 bohr)×(0.529177 Å/bohr) = 1.408 Å to a reasonable number of figures as in Fig. 6.12.

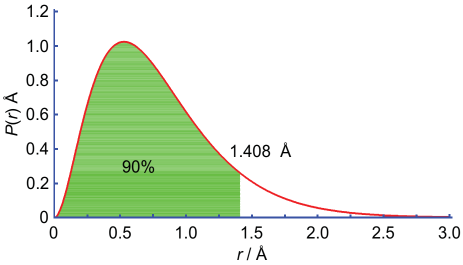


Figure 6.12: 1s H-atom atomic orbital distance at 90% of the total probability.

The drawing of the conventional 3-D contour surface diagram of the 1s atomic orbital is in Fig. 6.13. Molecular orbitals and other atomic orbitals use the same convention of the 90% contour of their own distribution function.

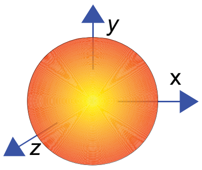


Figure 6.13: 1s H-atom AO 90% total probability contour surface.

Return to Question 2 (see page 84)

6.2.3 SOLUTION 3: THE AVERAGE KINETIC ENERGY OF GAS MOLECULES

$$(1)\quad \langle T_x \rangle = \int_{c_x=-\infty}^{c_x=+\infty} \frac{1}{2} m c_x^2 \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-m c_x^2/2k_B T}\, dc_x$$

$$(2)\quad u = \left(\frac{m}{2k_B T}\right)^{1/2} c_x \qquad (3)\quad u^2 = \frac{m c_x^2}{2k_B T} \qquad (4)\quad du = \left(\frac{m}{2k_B T}\right)^{1/2} dc_x$$

$$(5)\quad \langle T_x \rangle = \frac{k_B T}{\sqrt{\pi}} \int_{u=-\infty}^{u=+\infty} u^2 e^{-u^2}\, du \qquad (6)\quad \int_{x=-\infty}^{x=+\infty} x^2 e^{-x^2}\, dx = \frac{1}{2}\sqrt{\pi}$$

The integral (1) is the average translation energy of the gas molecules in one-dimension. We can evaluate the integral by using the suggested substitution (2) and squaring it in (3) and taking the derivative of (2) in (4). We substitute (3) and (4) into the integral (1) noting the change in the limits to give (5). Using the suggested standard integral (6) gives us the average kinetic energy of gas molecules in *one*-dimension ($R = N_A k_B$).

$$\langle T_x \rangle = \overbrace{\frac{1}{2} k_B T}^{\text{per molecule}} = \overbrace{\frac{1}{2} R T}^{\text{per mole}}$$

Average kinetic energy in one-dimension

Return to Question 3 (see page 86)

6.2.4 SOLUTION 4: TRAPEZIUM RULE INTEGRATION OF HEAT CAPACITY DATA TO CALCULATE ENTROPY

$$C_p = aT^3 \qquad a = \frac{13.01\ \mathrm{J\,K^{-1}\,mol^{-1}}}{(23\ \mathrm{K})^3} \qquad a = 1.069\times10^{-3}\ \mathrm{J\,K^{-4}\,mol^{-1}}$$

From the Debye T-cubed law we can calculate the constant (a) using $C_p = 13.01\ \mathrm{J\,K^{-1}\,mol^{-1}}$ at 23 K.

$$S(23\mathrm{K}) = \int_{T=0}^{T=23} \frac{C_p}{T}\, dT = \int_{T=0}^{T=23} \frac{aT^3}{T}\, dT = \int_{T=0}^{T=23} aT^2\, dT = \left[\frac{aT^3}{3}\right]_{T=0}^{T=23}$$

$$S(23\mathrm{K}) = (1.069\times10^{-3}\ \mathrm{J\,K^{-4}\,mol^{-1}})(23\mathrm{K})^3/3 = 4.336\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

Substituting our calculated value for the parameter (a) into the analytical integration from 0 K to 23 K gives the entropy of solid benzene at 23 K, S(23 K).

The entropy contribution above 23 K is determined using the trapezium rule. Fig. 6.14 shows that the area under the red curve between the limits of a particular 'slice' is approximated by the sum of the areas of the rectangle and the triangle. The triangle and rectangle together make a trapezium which is a quadrilateral with two parallel sides. The approximation becomes better the narrower we make the slice with more data points, we then add the contributions from several slices to obtain the approximate area between the wider limits.

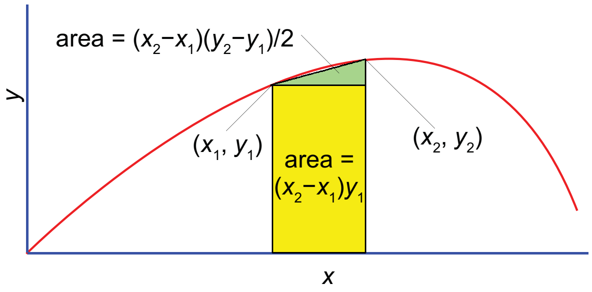


Figure 6.14: the trapezium rule.

$$\text{area of a trapezium} = (x_2 - x_1)\frac{(y_2 + y_1)}{2}$$

The area of a trapezium is the sum of the areas of the triangle and rectangle.

$$\int_{a}^{b} f(x)\,\mathrm{d}x \approx \sum_{k=1}^{N} (x_{k-1} - x_k)\frac{(y_{k-1} + y_k)}{2}$$ Trapezium rule for non-uniform trapezia

The definite integral between the limits *a* to *b* is approximately equal to the sum of the various trapeziums of non-uniform widths from *k* = 1 to *N*. The great advantage of the trapezium rule is that it is ideal for spreadsheet evaluation but the approximation improves with the number of data points.

	A	B	C	D	E	F	G	H	I
1	*T* / *K*	23.000	48.000	73.000	123.000	173.000	223.000	273.000	
2	*C*(*p*) / (J / K / mol)	13.010	29.660	40.460	55.440	74.060	97.610	122.300	
3	(*C*(*p* / *T*) / (J / K^2 / mol)	0.566	0.618	0.554	0.451	0.428	0.438	0.448	
4	Trapezium area		14.795	14.652	25.124	21.971	21.645	22.142	120.329

Figure 6.15: spreadsheet data from the integration using the trapezium rule.

The temperature and heat capacity data in rows 1 and 2 are entered manually. Cell B3 is entered as =B2/B1 and B2 is then selected and copied along the row from C3 to H3. Cell C4 is entered as =(C1–B1)*(C3+B3)/2 and selected and copied along the row D4 to H4. The sum of the trapeziums is in cell I4 is =SUM(C4:H4). The trapezium rule entropy of benzene between 23 K and 273 K is 120.329 J K^{-1} mol^{-1}.

It is best practice to always draw a graph of the data (Fig. 6.16) to check whether you have made a simple error in processing the raw data or if there is a 'rogue' experimental point which should be remeasured.

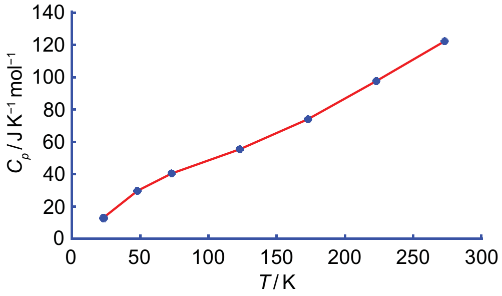


Figure 6.16: C_p against *T* for solid benzene.

The entropy of solid benzene at 273 K is the sum of the contributions from 0-23 K and 23-273 K and is *S*(273) = 4.336 + 120.329 = 124.7 J K^{-1} mol^{-1} using a combination of the Debye *T*-cubed law for analytical integration and the trapezium rule numerical integration for the entropy of solid benzene.

Return to Question 4 (see page 87)

6.2.5 SOLUTION 5: POLYNOMIAL INTEGRATION FOR THE ENTROPY OF BENZENE FROM HEAT CAPACITY DATA

We have to be very careful about fitting a polynomial to a set of data. First, remember a polynomial does not model the physical situation, it is only a mathematics method of manipulating the data. Secondly and more importantly, you should only fit a polynomial to 'smooth' data, those with gently changing values.

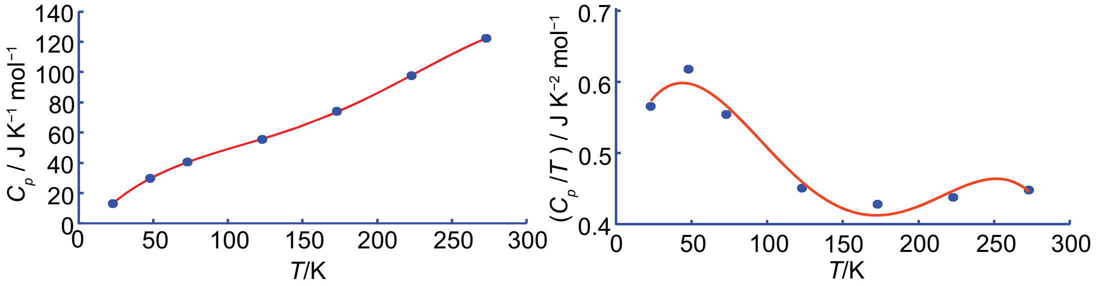


Figure 6.17: C_p versus T (left), and C_p/T versus T (right) for solid benzene.

The original experimental data is heat capacity and temperature. Fig. 6.17 (left) shows that the original data are smooth and a fourth-order polynomial gives a good fit with a goodness of fit value close to unity $R^2 = 0.99995$ to five decimal places. For clarity I have not included the units of the polynomial coefficients which are rounded to four decimal places.

$$C_p = -6.8065\times10^{-8}T^4 + 4.5660\times10^{-5}T^3 - 0.0100T^2 + 1.2024T - 9.7920$$

On the other hand you might be tempted to plot C_p/T against T and fit a polynomial to the values. As Fig. 6.17 (right) shows a fourth-order polynomial is a very poor fit and higher and lower order polynomials are even worse fits. Why is this? It is due to dividing by the temperatures which are relatively large numbers to give us ratios which are small quantities and results in a plot which is not smooth. Generally it is usually better to use the original experimental data rather than partially processed data.

$$(1)\quad \Delta S = \int_{23}^{273} -6.8065\times10^{-8}T^3 + 4.5660\times10^{-5}T^2 - 0.0100\,T + 1.2024 - 9.7920\,T^{-1}\,\mathrm{d}T$$

$$(2)\quad \Delta S = \left[\frac{-6.8065\times10^{-8}T^4}{4}\ \frac{+4.566\times10^{-5}T^3}{3}\ \frac{-0.01T^2}{2} + 1.202\,T - 9.792\ln T\right]_{23}^{273}$$

$$(3)\quad \Delta S = \frac{-6.8065\times10^{-8}(273^4-23^4)}{4}\ \frac{+4.566\times10^{-5}(273^3-23^3)}{3}$$

$$\frac{-0.01(273^2-23^2)}{2} + 1.202(273-23) - 9.792\ln\left(\frac{273}{23}\right)$$

$$(4)\quad \Delta S = -94.5132 + 309.4873 - 370 + 300.5 - 24.2252$$

The polynomial is substituted for C_p in (1) where each term has been divided by T. The definite integral (2) between 23 K to 273 K is evaluated in (3) and (4).

$$\Delta S(23-273\ \mathrm{K}) = 121.2\ \mathrm{J\,K^{-1}mol^{-1}}$$

Including the Debye T-cubed law value for S(23 K) (section 6.2.4) the present polynomial fit gives for the entropy of solid benzene $S(273) = 4.336 + 121.2 = 125.5$ J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$. In section 6.2.4 using the numerical integration by the trapezium rule gave $S(273) = 124.7$ J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$. The two methods agree within about ±0.3% which is reasonable. In this example the numerical trapezium rule had rather wide 'strips' and hence would be expected to be less precise than the line integral method. But on the other hand care is needed in using a polynomial fit which should only be used with smooth data.

Return to Question 5 (see page 88)

7 WEEK 7 CHEMISTRY AND PROBABILITY

Probability theory provides the theoretical models and analytical tools for the organization, interpretation and analysis of experimental chemical data. It is also used in various branches of chemistry to describe the collective behaviour of very large numbers of molecules or atoms. Also, by its very nature a wavefunction is related to the probability of finding a particle (an electron, atom, ion or molecule) in a certain position in space. These various aspects are covered in Week 7 and Week 8.

In order to obtain a measure of the expected spread of measurements (or reproducibility) of our experimental measurements, we calculate the standard deviation σ_y of a variable y. The first step is to calculate the average or mean value of our measurement $<y>$ where the average value is the sum of its observed values y_i divided by the number of observations n.

$$<y> = \frac{1}{n}\sum_{i=1}^{n} y_i \qquad \text{Average or mean value of a quantity}$$

We calculate how each data point varies from the mean of the data (y_i – <y>) which is called the residual R of an individual data point.

$$R = (y_i - <y>)$$

Squaring the residuals has the effect of treating results which are less than the mean the same as those which are greater than the mean and is called the square of the residuals SR.

$$SR = (y_i - <y>)^2$$

The effect of the deviations from *all* the individual data points is measured by the sum of squares of the residuals SSR.

$$SSR = \sum_{i=1}^{n} (y_i - <y>)^2$$

The standard deviation σ of all the n data points is defined below. This residuals treatment is ideal for handling with a spreadsheet as we see in section 7.1.1.

$$\sigma_y = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n} (y_i - <y>)^2} \qquad \sigma_y = \sqrt{\frac{1}{n-1}SSR}$$ Standard deviation of n data points

If the calculated quantity y is a function of several variables a, b, c… that is $y = f(a, b, c…)$ the square of the standard deviation σ_y^2 (called the variance) is related to the variances of (a, b, c) and is given by the error propagation equation or variance equation.

$$\sigma_y^2 = \left(\frac{\partial y}{\partial a}\right)^2 \sigma_a^2 + \left(\frac{\partial y}{\partial b}\right)^2 \sigma_b^2 + \left(\frac{\partial y}{\partial c}\right)^2 \sigma_c^2 + \ldots$$ Error propagation or variance equation

Where $\partial y/\partial a$ (pronounced 'del y by del a') means the partial derivative, that is the differential of y with respect to a but treating the other variables b, c… as constants for this partial derivative. The other partial derivatives are each treated in an equivalent fashion.

Perhaps the most important and one of the commonest tasks we face is fitting the best line to a graph from a lab experiment that we have carried out. These aspects of curve fitting are covered in Chemistry Maths 3 of this series (Parker 2013, a new edition due out in 2019) which begins with linear and non-linear curve fitting of experimental data.

7.1 WEEK 7 TUTORIAL QUESTIONS

7.1.1 QUESTION 1: TRACE ANALYSIS BY ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption spectroscopy (AAS) is an instrumental technique used for the quantitative determination of trace and ultra-trace levels of elements in a variety of samples. For example, measurement of various metals in water and drinks, in food, in blood analysis, in river and environmental protection. In scientific archaeology and forensic science the composition of trace elements of teeth and bones, metal, pottery, or glass gives information on their geographical origins. Fig. 7.1 shows a schematic diagram of the AAS instrument which you might use in your lab classes.

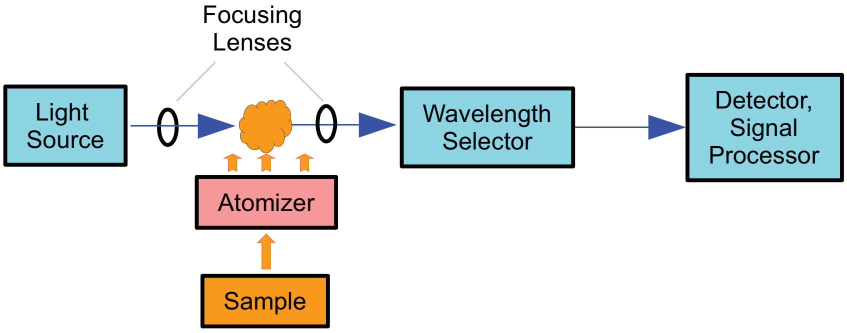
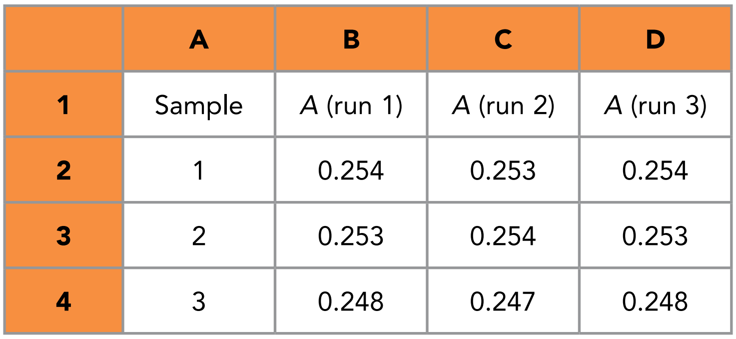


Figure 7.1: Schematic atomic absorption spectrometer.

The atomizer which vaporizes the sample and also converts it to atoms is commonly a high temperature flame or a hot graphite tube. Atoms absorb light at specific wavelengths due to quantum mechanics and hence the absorption at the chosen wavelength leads to a measure of the absorbance of that wavelength. Once the AAS apparatus has been calibrated with known concentration samples we can use the absorbance value of the unknown sample to calculate the concentration of the atoms of the element which we are investigating.

Chromium(VI) is toxic to animals and plants. It is present in natural waters in sub-trace level and its determination requires separation from the less toxic chromium(III) and pre-concentration of the solution. Absorbance values, which are pure numbers, obtained for Cr(VI) solutions using the chromium resonance line at λ = 357.9 nm are reported below. Fig. 7.2 three different samples of the water were taken and measured in three different times by AAS analysis.



	A	**B**	**C**	**D**
1	Sample	A (run 1)	A (run 2)	A (run 3)
2	1	0.254	0.253	0.254
3	2	0.253	0.254	0.253
4	3	0.248	0.247	0.248

Figure 7.2: spreadsheet of absorbances for AAS analysis.

Determine the average absorbance of all nine measurements and the square of the nine residuals SR. Calculate the sum of the square of the nine residuals SSR. Find the standard deviation and the percent relative standard deviation, defined as the standard deviation divided by the average value $\sigma_y/<y>$.

Jump to Solution 1 (see page 108)

7.1.2 QUESTION 2: SOLUBILITY PRODUCT AND ERROR PROPAGATION

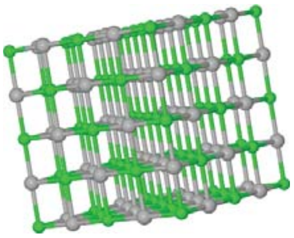


Figure 7.3: silver chloride crystal.

Silver chloride AgCl is a white solid which is only slightly soluble in water, so there is a heterogeneous two-phase equilibrium of solid AgCl and a saturated solution of Ag^+ and Cl^- ions in water.

$$\mathrm{AgCl(s)} \rightleftarrows \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

The equilibrium constant should be given in terms of the activities (a) of the two ions and the solid. For these sparingly soluble salts the ionic concentrations are small and we may replace the activities of the ions by the molar concentrations divided by their standard states $c°$.

$$(1)\quad K = \frac{\dfrac{[\mathrm{Ag^+(aq)}]\,\mathrm{mol\,L^{-1}}}{c^\circ}\;\dfrac{[\mathrm{Cl^-(aq)}]\,\mathrm{mol\,L^{-1}}}{c^\circ}}{\dfrac{[\mathrm{AgCl(s)}]\,\mathrm{mol\,L^{-1}}}{c^\circ}}$$

$$(2)\quad K = \frac{[\mathrm{Ag^+(aq)}]\,\mathbf{mol\,L^{-1}}}{\mathbf{1\,mol\,L^{-1}}}\;\frac{[\mathrm{Cl^-(aq)}]\,\mathbf{mol\,L^{-1}}}{\mathbf{1\,mol\,L^{-1}}}$$

The equilibrium constant for the reaction of the slightly soluble solid dissolving in the solvent is (1). In (1) the standard state for any pure solid or pure liquid such as AgCl (solid) is unity and so the concentration of any pure solid or pure liquid does not appear in the denominator of the equilibrium constant in (2). For instance in our example of a saturated solution then adding more solid AgCl will not make the solution 'more saturated' the added pure solid will just sit at the bottom of the solution along with the rest of the solid.

In (2) each ionic concentrations are divided by their standard state which is $c° = 1$ mol L^{-1} shown in red and so the units cancel out for each of the ionic species. This modified version of (2) is called the solubility product and is written as follows, but remember these are dimensionless 'concentrations' as the units have been cancelled out by division with the standard state. So a solubility product (or any equilibrium constant) is dimensionless.

$$K_{\mathrm{sp}} = [\mathrm{Ag^+(aq)}][\mathrm{Cl^-(aq)}]$$ Solubility product or solubility constant of silver chloride

The solubility s of each of the ionic species has units [Ag^{+}(aq) mol L^{-1}] and [Cl^{-}(aq) mol L^{-1}] as they are not divided by their standard state.

$$s = [\mathrm{Ag}^{+}\,(\mathrm{aq})\,\mathrm{mol\ L}^{-1}] = [\mathrm{Cl}^{-}\,(\mathrm{aq})\,\mathrm{mol\ L}^{-1}]$$ Solubility of Ag^{+} or Cl^{-} in a saturated solution

Thus the solubility product for our univalent-univalent ions saturated solution of AgCl is written as follows $K_{sp} = s^2/(\mathrm{mol\ L}^{-1})^2$ or $K_{sp} = s^2/(\mathrm{mol}^2\ \mathrm{L}^{-2})$ and $s = K_{sp}{}^{1/2}$ (mol L^{-1}).

Using the error propagation formula determine the solubility s and its standard deviation σ_s also the relative standard deviation σ_s/s if the solubility product of AgCl is $K_{sp} = (1.8 \pm 0.2)\times10^{-10}$ at 25°C.

Jump to Solution 2 (see page 109)

7.1.3 QUESTION 3: WAVEFUNCTIONS AND PROBABILITY

We are going to use the particle in a box model to estimate the transition energies in a conjugated molecule such as a dye molecule. The π-electrons move along the length of the carbon conjugated backbone of the molecule. We may treat this situation as a 'one-dimensional' box confining the electrons, see section 4.2.2. For example β-carotene (Fig. 7.4) is the red pigment found in carrots and many other fruits and vegetables. Its conjugated double bond structure enables it to absorb at the blue end of the visible spectrum, hence it appears red.

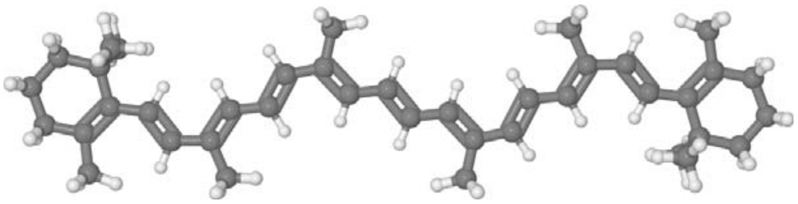


Figure 7.4: β-carotene, grey H, dark grey C.

For a particle of mass m confined between two walls which are at $l = 0$ and $l = L$, the quantized energy E of the particle may only have following set of values.

$$E = \frac{n^2 h^2}{8 m L^2} \qquad n = 1,2,3,\ldots$$ Energy of a particle in a one-dimensional box

The quantum number n may take the values $n = 1, 2, 3\ldots$ The wavefunction of the trapped particle is shown below where the angle is in *radians.*

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n \pi l}{L}$$ Normalized wavefunction for a particle in a one-dimension box

The probability P of finding the particle in a specified region of space is the integral of the squared of the wavefunction over that region of space.

If an electron is confined to a box of length L = 1.0 nm (roughly seven carbon atoms long) calculate the probability that when it is in the ground state (n = 1) the electron is found in the region between the end of the molecule l = 0 nm and l = 0.2 nm. Use the substitution $\sin^2(kx) = (\frac{1}{2} - \frac{1}{2}\cos(2kx))$ and note that $\sin 2(kx)$ is the conventional way of writing $(\sin\ kx)^2$.

Jump to Solution 3 (see page 110)

7.2 WEEK 7 TUTORIAL SOLUTIONS

7.2.1 SOLUTION 1: TRACE ANALYSIS BY ATOMIC ABSORPTION SPECTROSCOPY

	A	B	C	D	E	F	G	H	I	J
1	Sample	*A* (run 1)	*A* (run 2)	*A* (run 3)	<*A*>	*SR* (run 1)	*SR* (run 2)	*SR* (run 3)	*SSR*	σ_A
2	1	0.254	0.253	0.254	0.252	5.975E-06	2.086E-06	5.975E-06	7.022E-05	2.963E-03
3	2	0.253	0.254	0.253		2.086E-06	5.975E-06	2.086E-06		
4	3	0.248	0.247	0.248		1.264E-05	2.075E-05	1.264E-05		

Figure 7.5: spreadsheet analysis of chromium(VI) AAS absorbances.

In Fig. 7.5 all the cell are displayed to three decimal points for clarity. The average of all nine absorbances <*A*> is calculated in cell E2 as =SUM(B2:D4)/9 and is <*A*> = 0.252.

The squares of the residuals *SR* are calculated, for example cell F2 is = (B2-E2)^2 and then F2 is copied from F2 to H4. Note the average value remains fixed as E2 is used with dollar signs E2.

The sum of the squares of the residuals *SSR* in cell I2 is =SUM(F2:H4) and is equal to 7.022×10^{-5} and thus the standard deviation in cell J2 is calculated as =SQRT((1/(9-1))*I2) note the use of brackets to make the calculation the same as what you set out to calculate. The standard deviation of the absorbances is $\sigma_A = 2.963\times10^{-3}$. In your lab note book you would then quote your measurements as the atomic spectroscopy absorbance of Cr(VI) present in the water samples is 0.252 ± 0.003.

The result and the precision are both quoted to the same powers of ten and the *first* decimal place of the precision (rounded if necessary) determines the *last* decimal place of the result (also rounded as necessary). Knowing the sensitivity of the AAS to the Cr(VI) from the calibration experiments and thus the extinction coefficient at this wavelength, the analytical chemist would then calculate the concentration of the pollutant.

As experimentalists, the scientist is also interested in finding the *relative standard deviation*, the standard deviation divided by the average value, σ_A/<*A*> to find out the quality of the experimental method and equipment. The relative standard deviation is (0.003/0.252)×100 = 1.2%. You could now change your experimental procedure and perhaps equipment to see whether the relative standard deviation can be improved or whether it deteriorates.

Return to Question 1 (see page 103)

7.2.2 SOLUTION 2: SOLUBILITY PRODUCT AND ERROR PROPAGATION

The solubility of the silver ions and chloride ion are calculated from the square root of the solubility product.

$$s = K_{\text{sp}}^{1/2}(\text{mol L}^{-1}) = (1.8\times10^{-10})^{1/2}(\text{mol L}^{-1}) = 1.3416\times10^{-5}\ \text{mol L}^{-1}$$

Although the square root has a positive and negative value, only the positive solubility is chemically sensible. I have deliberately retained extra decimal places for the moment, to reduce later rounding errors. This will be corrected when we have the standard deviation.

$$(1)\quad \sigma_s^2 = \left(\frac{\text{d}\,s}{\text{d}\,K_{\text{sp}}}\right)^2 (\sigma_{K_{\text{sp}}})^2 \qquad (2)\quad \sigma_s = \left(\frac{\text{d}\,s}{\text{d}\,K_{\text{sp}}}\right)\sigma_{K_{\text{sp}}}$$

$$(3)\quad \sigma_s = \frac{1}{2}K_{\text{sp}}{}^{-1/2}\,\sigma_{K_{\text{sp}}} \qquad (4)\quad \sigma_s = \frac{1}{2}\,\frac{\overbrace{0.02\times10^{-10}\ \text{mol L}^{-1}}^{\sigma_{K_{sp}}}}{\underbrace{(1.8\times10^{-10})^{1/2}}_{K_{sp}^{1/2}}}$$

$$(4)\quad \sigma_s = 7.4536\times10^{-8}\ \text{mol L}^{-1} \qquad (6)\quad s = (1.342\pm0.007)\times10^{-5}\ \text{mol L}^{-1}$$

The error propagation formula (1) for this simple one independent variable, means that the partial derivatives become a full derivative. For this one-variable case we may then take the square roots (2) on each side of the error propagation equation. The derivative is (3) and substitution of the variables (4) allows the standard deviation of the solubility to be calculated in (5). The solubility may now be quoted to the correct number of decimal places in (6).

$$\frac{\sigma_s}{S} = \frac{7.4536\times10^{-8}\ \text{mol L}^{-1}}{1.342\times10^{-5}\ \text{mol L}^{-1}} = 5.5541\times10^{-3}\approx0.56\%$$

The relative standard deviation is calculated and relative precision is about 0.56% which could possibly be improved.

Return to Question 2 (see page 105)

7.2.3 SOLUTION 3: WAVEFUNCTIONS AND PROBABILITY

(1) $$\psi_1 = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi}{L}l\right)$$

(2) $$P = \frac{2}{L}\int_{l=0}^{l=0.2}\sin^2\left(\frac{\pi}{L}l\right)\,\mathrm{d}l$$

(3) $$P = \frac{2}{L}\int_{l=0}^{l=0.2}\frac{1}{2}-\frac{1}{2}\cos\left(\frac{2\pi}{L}l\right)\,\mathrm{d}l$$

(4) $$P = \frac{2}{L}\left[\frac{l}{2}-\frac{L}{4\pi}\sin\left(\frac{2\pi}{L}l\right)\right]_{l=0}^{l=0.2}$$

(4) $$P = 0.2 - \frac{1}{2\pi}\sin(0.4\pi)$$

(6) $$P = 0.04863$$

The normalized wavefunction of the electron in the ground state $n = 1$ is (1). The probability P of the electron being between $l = 0$ and $l = 0.2$ nm is the integral (2) of the square of the ground state wavefunction between these limits. To evaluate the integral (2) we make use in (3) of the trigonometric relationship $\sin^2(kx) = (½ - ½\cos(2kx))$ where $k = \pi/L$ and $x = l$. Integration gives the definite integral (4). Inserting the upper limits and the length of the box $L = 1$ nm gives (5). In (6) when using your calculator remember the sine is in *radians* not degrees. The probability of the electron being between 0 and 0.2 nm is 0.04863 or about 4.86%.

Fig. 7.6 plots the normalized wavefunction for the fundamental standing wave and the probability density of the square of the wavefunction. That is the probability that the electron is between 0 and 0.2 nm is the area under the probability curve between these limits which the 'Graph' spreadsheet (Johansen, 2013) calculates as 4.86% of the total probability agreeing with our integration. Notice how the wavefunction is a sine curve but the square of the wavefunction is 'bell' shaped.

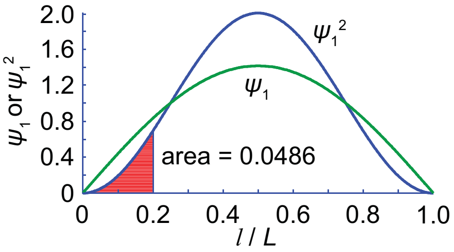


Figure 7.6: wavefunction and probability density of a particle in a 1-D box.

Return to Question 3 (see page 106)

8 WEEK 8 CHEMISTRY AND PROBABILITY

8.1 WEEK 8 TUTORIAL QUESTIONS

8.1.1 QUESTION 1: THE BOLTZMANN DISTRIBUTION AND QUANTUM ENERGY LEVELS

The Boltzmann distribution allows us to determine the distribution of molecules amongst quantized energy levels, i.e. the population of the various quantum levels. Fig. 8.1 is a schematic of the thermal equilibrium distribution of molecules over non-degenerate levels with equal energy gaps. Depending upon the type of energy we are considering, the zero of energy may coincidence with the lowest quantum level. Don't confuse this quantum based Boltzmann distribution with the Maxwell-Boltzmann distribution which deals with the non-quantized (classical) translational motion of ideal gas molecules.

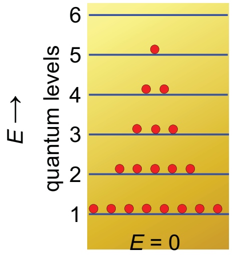


Figure 8.1: a population distribution of molecules.

$$\frac{N_i}{N} = \frac{\mathrm{e}^{-E_i/k_\mathrm{B}T}}{\sum_i \mathrm{e}^{-E_i/k_\mathrm{B}T}}$$ Boltzmann distribution of molecules in non-degerate energy levels

For non-degenerate energy levels where N is the total number of molecules and N_i is the number of molecules in state i with energy E_i then the ratio of N_i to the total number of molecule N is given by the Boltzmann distribution. Where k_B is Boltzmann's constant and the summation is over all the allowed quantum energy levels.

Determine the expression for the number of molecules occupying level i relative to those in level j, that is find the population ratio N_i/N_j of molecules in the two different non-degenerate quantum levels i and j.

Jump to Solution 1 (see page 116)

8.1.2 QUESTION 2: POPULATIONS OF MOLECULES IN TRANSLATIONAL, ROTATIONAL, VIBRATIONAL, AND ELECTRONIC ENERGY LEVELS

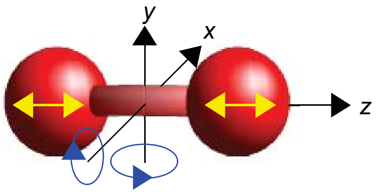
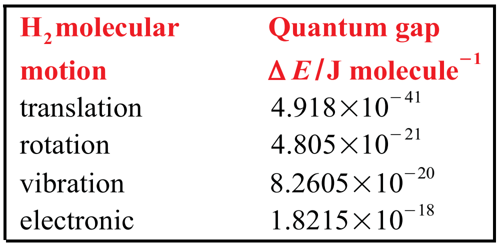


Figure 8.2: a diatomic molecule's rotations and bond vibration.

A diatomic molecule can undergo the following types of motion. (1) Translational motion, the movement of the whole molecule through space which may be resolved into components along the x, y, and z Cartesian coordinates. (2) Rotational motion, the molecule rotates around the centre of mass which for a diatomic molecule may be resolved into two components of rotation around the x-axis and y-axis. (3) Vibrational motion, the bond length increases and decreases along the z-axis. (4) An electron may be excited and jump to an excited electronic energy level.

The energy differences ΔE between the first excited level u and the ground state g for translation, rotation, vibration, and electronic energies are listed in Fig. 8.3. Note that I have quoted the energy in J molecule^{-1} although this is strictly a non-SI unit (it should be just J) however it is very useful in reminding us that it is the energy per molecule.



H_2 molecular motion	**Quantum gap ΔE / J molecule^{-1}**
translation	4.918×10^{-41}
rotation	4.805×10^{-21}
vibration	8.2605×10^{-20}
electronic	1.8215×10^{-18}

Figure 8.3: quantum gaps for the H_2 molecule.

H_2 gas molecules at 298 K and 1 bar pressure are undergoing collisions on average about every 10^{-10} s. These collisions can cause the H_2 molecule to jump from its ground state to its first and other excited states, and also to lose energy and jump down a state. The H_2 molecules will quickly reach a thermodynamic equilibrium of populations characteristic of its temperature of 298 K.

Using the values for the energy gaps calculate the relative population N_u / N_g for the first excited state relative to the ground state at 298 K, for each of the 'motions' using your derived equation for the Boltzmann distribution of populations from section 8.1.1 and comment on your results. The Boltzmann constant is $k_B = 1.381 \times 10^{-23}$ J K^{-1}. We are assuming non-degenerate energy levels (Parker 2015, section 1.7.3) don't worry about this assumption about degeneracy, as it will be discussed later on in your chemistry course.

Jump to Solution 2 (see page 116)

8.1.3 QUESTION 3: MAXWELL-BOLTZMANN DISTRIBUTION OF THE SPEEDS OF GAS MOLECULES

From section 8.2.2 we have seen that translational motion of molecules may be accurately treated as a classical non-quantized motion. The probability that the molecules of mass m at a temperature T have a speed between c and c+dc is equal to $P(c, c+dc) = f(c)\,dc$. Where $f(c)$ is the Maxwell-Boltzmann speed distribution in three-dimensions. The conventional symbol for speed is c as it is less likely to be confused with velocity or frequency. If the molecules have a mass of m kg (per molecule) they have a molar mass of M kg mole^{-1}. The Maxwell-Boltzmann distribution may written in two equivalent ways.

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

$$f(c) = 4\pi\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} c^2 \mathrm{e}^{-mc^2/2k_\mathrm{B}T}$$

Maxwell-Boltzmann distribution in 3-D

Remember the SI unit of mass is the kilogram *not* the gram and R is the gas constant and k_B is Boltzmann's constant.

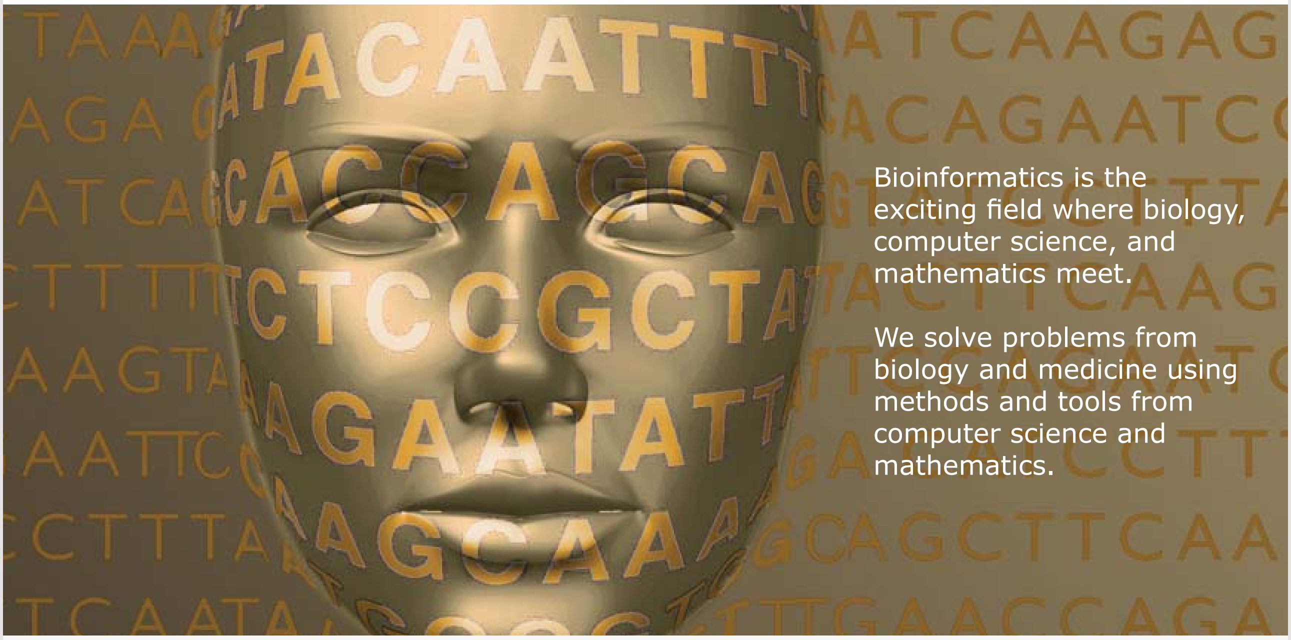
Calculate the most probable speed c_mp at 298.15 K of $^{14}\mathrm{N}_2$ using the relationship below where the molar mass of $^{14}\mathrm{N}_2$ is $M = 28.02\ \mathrm{g\ mol^{-1}}$.

$$c_\mathrm{mp} = \sqrt{\frac{2RT}{M}}$$

Most probable speed for the Maxwell-Boltzmann speed distribution

Estimate the fraction and then the number of molecules per centimetre cubed which have velocities which exceed the most probable speed by up to 1% given that the total number of molecules is 9.00×10^{24} molecules $\mathrm{cm^{-3}}$.

Jump to Solution 3 (see page 119)



8.2 WEEK 8 TUTORIAL SOLUTIONS

8.2.1 SOLUTION 1: THE BOLTZMANN DISTRIBUTION AND QUANTUM ENERGY LEVELS

To obtain an expression for the number of molecules in level *i* relative to that of level *j* we write two separate populations for energy levels *i* in (1) and *j* in (2).

$$(1)\quad \frac{N_i}{N} = \frac{e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \qquad (2)\quad \frac{N_j}{N} = \frac{e^{-E_j/k_B T}}{\sum_j e^{-E_j/k_B T}}$$

$$(3)\quad \sum_i e^{-E_i/k_B T} = \sum_j e^{-E_j/k_B T} \qquad (4)\quad \frac{N_i\ N}{N_j\ N} = \frac{e^{-E_i/k_B T}}{e^{-E_j/k_B T}}$$

The sum over *all* quantum levels *i* and *all* quantum levels *j* are the same (3), all we were doing is using a different symbol for counting the levels. In equation (4) for the ratio of N_i and N_j the total number of molecules N cancels. The exponentials in expression (4) may be simplified as the ratio of two exponential terms is equal to the exponential of the difference of the two terms, so we replace the ratio exp(*i*)/exp(*j*) by exp(*i* – *j*).

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/k_B T}$$ Ratio of the number of molecules in non-degenerate energy levels

The ratio of the populations is the negative exponential of the energy gap between them compared with the energy $k_B T$.

Return to Question 1 (see page 112)

8.2.2 SOLUTION 2: POPULATIONS OF MOLECULES IN TRANSLATIONAL, ROTATIONAL, VIBRATIONAL, AND ELECTRONIC ENERGY LEVELS

Fig. 8.4 shows a schematic view of the various energy levels in a typical diatomic molecule with the spacing of the rotational levels *J* and vibrational levels *v* not to scale for clarity. For historical reasons the single prime indicates levels of the upper electronic state, whilst double prime indicates a lower electronic state.

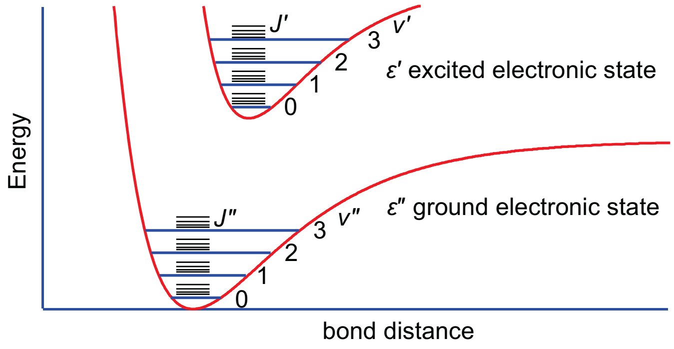


Figure 8.4: potential curves and energy levels for a diatomic molecule, not to scale.

$$\frac{N_u}{N_g} = \mathrm{e}^{-(E_u - E_g)/k_\mathrm{B}T}$$

We use the Boltzmann ratio of populations of molecules in two energy levels from section 8.2.1. The relative populations are determined by substituting ΔE values from section 8.1.2, with T =298 K and Boltzmann's constant k_B = 1.381×10^{-23} J K^{-1}.

$$\frac{N_u^\mathrm{T}}{N_g^\mathrm{T}} = \mathrm{e}^{-(4.918\times10^{-41}\,\mathrm{J})/(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})} = 1 \quad \text{H}_2 \text{ translational levels}$$

For translational motion we obtain a ratio of unity to *at least* 9 significant figures. The energy gap for translational motion is negligible (~5×10^{-41} J) compared to the size of $k_\mathrm{B}T$ = 4.115×10^{-21} J at 298 K, where $k_\mathrm{B}T$ is a measure of the average thermal energy per molecule. To a very good approximation we may treat the translational motion as non-quantized as long as the containing vessel is of macroscopic size ('infinite' compared with atomic dimensions). This is the whole basis behind the classical treatment by the Maxwell-Boltzmann distribution of translational velocities (sections 8.1.3 and 8.2.3). The value of the translational energy gap for H_2 was calculated using the energy of a particle in a box and making the box have sides of 1 metre, a macroscopic or normal sized container for the gas (Parker 2015, section 1.7.4).

$$\frac{N_u^\mathrm{R}}{N_g^\mathrm{R}} = \mathrm{e}^{-(4.805\times10^{-21}\,\mathrm{J})/(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})} = 0.3111 \quad \text{H}_2 \text{ rotational levels}$$

The ratio of energy gap for the rotational motion of H_2 to the measure $k_\mathrm{B}T$ of thermal energy is slightly larger than unity ~1.7. There are about 30 molecules in the excited rotational level (J = 1) for every 100 molecules in the ground rotational level (J = 0).

$$\frac{N_u^\mathrm{V}}{n_g^\mathrm{V}} = \mathrm{e}^{-(8.2605\times10^{-20}\,\mathrm{J})/(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})} = 1.917\times10^{-9} \quad \text{H}_2 \text{ vibrational levels}$$

The H_2 bond length extends and contracts around its average equilibrium bond length. The energy gap to the excited vibrations level is ~20 times larger than $k_B T$. A negligible fraction of H_2 molecules are in the excited vibrational level (v = 1) at 298 K, to a very good approximation all the H_2 molecules are in their ground vibrational level (v = 0) at 298 K.

$$\frac{N_u^{\mathrm{E}}}{N_g^{\mathrm{E}}} = \mathrm{e}^{-(1.8215\times10^{-18}\,\mathrm{J})/(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})} \approx 0 \qquad \text{H}_2\text{ electronic levels}$$

The thermal population of the first excited electronic state (ε' = 0) of H_2 is zero to at least nine significant figures. This arises from the electronic gap being ~400 times larger than the thermal energy for H_2. A similar situation occurs with *most* other molecules.

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8.2.3 SOLUTION 3: MAXWELL-BOLTZMANN DISTRIBUTION OF THE SPEEDS OF GAS MOLECULES

$$c_{\mathrm{mp}} = \sqrt{\frac{2RT}{M}} \qquad c_{\mathrm{mp}} = \sqrt{\frac{2\times(8.3145\ \mathrm{J\,K^{-1}mol^{-1}})\times(298.15\ \mathrm{K})}{28.02\times10^{-3}\ \mathrm{kg\,mol^{-1}}}} \qquad c_{\mathrm{mp}} = 420.6\ \mathrm{m\,s^{-1}}$$

The units cancel correctly in the above calculation as we have replaced the named unit 'joule' by the base units of J = kg m^2 s^{-2}. The most probable speed is the maximum of the speed distribution curve which is 420.6 m s^{-1} or 940.9 miles per hour. The $^{14}N_2$ molecules are really moving fast at room temperature and this is typical of gas-phase low-mass molecules at 25 °C. Remember that molecules only travel on average short distances between collisions at normal atmospheric pressures. This is due to the rapid collisions with other molecules and the walls of the container occurring about every 10^{-10} s (at normal pressures).

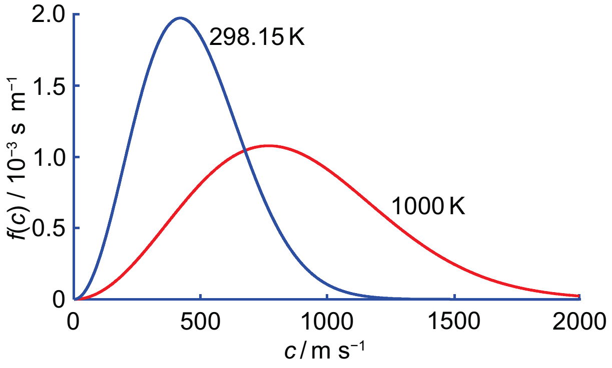

Figure 8.5: Maxwell-Boltzmann speed distributions for N_2 at 298.15 and 1000 K.

Fig. 8.5 shows the distributions of speeds for the nitrogen molecules at 298.15 K and at 1000 K. The distribution function is not symmetric but is skewed towards high speeds.

Secondly, we are interested in calculating the fraction of molecules whose velocity ranges between 420.6 m s^{-1} and 420.6 + 4.206 = 424.8 m s^{-1} is $P(c) = f(c)\mathrm{d}c$. The probability calculation below is split over 2 lines for clarity.

$$P(c) = f(c)\,\mathrm{d}c = 4\pi\left(\frac{28.02\times10^{-3}\ \mathrm{kg\,mol^{-1}}}{2\pi(8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\right)^{3/2}(420.6\ \mathrm{m\,s^{-1}})^2$$

$$\exp-\frac{(28.02\times10^{-3}\ \mathrm{kg\,mol^{-1}})(420.6\ \mathrm{m\,s^{-1}})^2}{2(8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\times\overbrace{(4.206\ \mathrm{m\,s^{-1}})}^{\mathrm{d}c}$$

The fraction of molecules with velocity between 420.6 m s^{-1} and 424.8 m s^{-1} is 0.008301 or 0.8301%, Fig. 8.6.

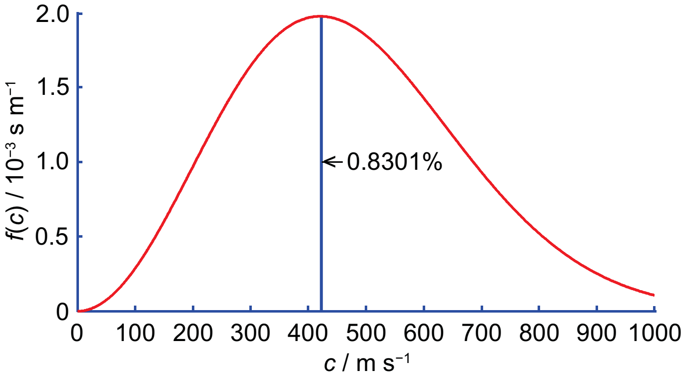

Figure 8.6: N_2 at 25°C probability of speed from c_{mp} to 1.01 × c_{mp}.

From this probability we can calculate the number of molecules by multiplying $f(c)\mathrm{d}c$ by the total number of molecules N_{tot}.

$$f(c)\,\mathrm{d}c \times N_{\text{tot}} = (8.301\times10^{-3})(9.00\times10^{24}\text{ molecules cm}^{-3})$$
$$f(c)\,\mathrm{d}c \times N_{\text{tot}} = 7.4709\times10^{22}\text{ molecules cm}^{-3}$$

Although the fraction of molecules is a small area under the curve, 0.8301%, the number density of molecules in this speed range is enormous, ~7×10^{22} per cm^3.

Return to Question 3 (see page 114)

Intermediate Maths for Chemists is followed by the final book in the series, *Advanced Maths for Chemists* (Parker 2013, new edition due in 2019) which completes the maths tools that a first year chemist or any chemistry based scientist or engineer would encounter during their undergraduate studies and later professional life.

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10 LIST OF FORMULAE

$$\overbrace{c}^{\text{physical quantity}} = \overbrace{2.9979\times10^{8}}^{\text{pure number}}\ \overbrace{\mathrm{m\,s^{-1}}}^{\text{units}}$$ Example of a physical quantity

$y = mx + c$ Equation of a straight line graph

$$f(x) = f(a) + (x-a)\frac{\mathrm{d}f(a)}{\mathrm{d}x} + \frac{(x-a)^2}{2!}\frac{\mathrm{d}^2 f(a)}{\mathrm{d}x^2} + \frac{(x-a)^3}{3!}\frac{\mathrm{d}^3 f(a)}{\mathrm{d}x^3} + \cdots$$ Taylor series

$$f(x) = f(0) + x\frac{\mathrm{d}f(0)}{\mathrm{d}x} + \frac{x^2}{2!}\frac{\mathrm{d}^2 f(0)}{\mathrm{d}x^2} + \frac{x^3}{3!}\frac{\mathrm{d}^3 f(0)}{\mathrm{d}x^3} + \ldots$$ Maclaurin series

$$E = \left(\frac{n_X^2}{L_X^2} + \frac{n_Y^2}{L_Y^2}\right)\frac{h^2}{8m}$$ Particle in a two-dimensional box

$$\frac{\mathrm{d}L_X}{\mathrm{d}L_Y} = -\frac{L_X^3/n_X^2}{L_Y^3/n_Y^2}$$ Altering the size of a quantum well at constant energy

$$P = \frac{4}{a_0^3}r^2\,\mathrm{e}^{-2r/a_0}$$ Radial distribution function for a 1s H-atom electron

$$\frac{\mathrm{d}(uv)}{\mathrm{d}x} = u\frac{\mathrm{d}v}{\mathrm{d}x} + v\frac{\mathrm{d}u}{\mathrm{d}x}$$ Product rule for differentiation

$$U^{\mathrm{V}} = nN_{\mathrm{A}}hc\bar{\upsilon}\frac{\mathrm{e}^{-hc\bar{\upsilon}\beta}}{1-\mathrm{e}^{-hc\bar{\upsilon}\beta}}$$ Vibrational internal energy of diatomic molecules

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{u}{v}\right) = \frac{v\left(\frac{\mathrm{d}u}{\mathrm{d}x}\right) - u\left(\frac{\mathrm{d}v}{\mathrm{d}x}\right)}{v^2}$$ Quotient rule for differentiation

$$C_V^{\mathrm{V}} = -k_{\mathrm{B}}\beta^2\frac{\mathrm{d}U^{\mathrm{V}}}{\mathrm{d}\beta}$$ Vibrational heat capacity for SHO diatomic molecules

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \frac{\mathrm{d}y}{\mathrm{d}z}\times\frac{\mathrm{d}z}{\mathrm{d}x}$$ Chain rule of differentiation

$a_0 = 0.5292\times10^{-10}\ \mathrm{m}$ The Bohr radius

$$C_V^{\mathrm{V}} = nR\left(\frac{hc\bar{\upsilon}}{k_{\mathrm{B}}T}\right)^2\frac{\mathrm{e}^{-hc\bar{\upsilon}/k_{\mathrm{B}}T}}{\left(1-\mathrm{e}^{-hc\bar{\upsilon}/k_{\mathrm{B}}T}\right)^2}$$ SHO contribution to heat capacity

$$V_{\text{stretch}} = \frac{1}{2}k_{\text{stretch}}(r-r_e)^2 \qquad V_{\text{bend}} = \frac{1}{2}k_{\text{bend}}(\theta-\theta_e)^2$$ SHO potential energy

$E_v = (v+½)h\nu$ Simple harmonic oscillator

$\nu = \frac{1}{2}\sqrt{\frac{k}{\mu}}$	Vibration frequency, μ is the effective mass
$E^{\mathrm{V}} = n N_{\mathrm{A}} h c \bar{\upsilon} \frac{\mathrm{e}^{-hc\bar{\upsilon}\beta}}{1-\mathrm{e}^{-hc\bar{\upsilon}\beta}}$	Total vibrational energy of n moles of diatomic molecules
$k t = \ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x}$	Integrated first-order rate law
$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}[\mathrm{I}]} = \frac{\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}}{\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}}$	Example of a parametric derivative
$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} \approx k_a [\mathrm{A}]_0$	S_N1 (substitution nucleophilic unimolecular) rate law
$F = m\frac{\mathrm{d}^2 x}{\mathrm{d}t^2}$	An ordinary differential equation, Newton's second law of motion
$a\frac{\mathrm{d}y}{\mathrm{d}x} + by + c = 0$	First-order ordinary differential equation
$a\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + b\frac{\mathrm{d}y}{\mathrm{d}x} + cy + d = 0$	Second-order ordinary differential equation
$J = -D\frac{\mathrm{d}c}{\mathrm{d}x}$	Fick's first law of diffusion
$<\Delta x^2>^{½} = \sqrt{2Dt}$	Einstein-Smoluchowski equation
$f(c) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} c^2 \mathrm{e}^{-Mc^2/2RT}$	Maxwell-Boltzmann speed distribution
$\frac{1}{[\mathrm{I}]} - \frac{1}{[\mathrm{I}]_0} = kt$	Integrated second-order rate law
$\log\frac{I_0}{I} = \varepsilon[\mathrm{A}]l$	Beer-Lamber law
$<c> = \left(\frac{8RT}{\pi M}\right)^{1/2}$	Maxwell-Boltzmann average speed of gas molecules
$-\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi$	Schrödinger equation for motion in one-dimension
$\psi = A\sin\left(\frac{2\pi m v}{h}x\right) + B\cos\left(\frac{2\pi m v}{h}x\right)$	General wavefunction for 1-D motion
$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$	Wavefunction of a particle confined in a 1-D box
$m_l\lambda = 2\pi r \qquad m_l = 0, \pm1, \pm2, \pm3\ldots$	Particle on a ring boundary condition

$$E = \frac{1}{2} m v^2$$

Quantum mechanics energy of the unconstrained motion of a particle

$$E = \frac{n^2 h^2}{8 m L^2} \qquad \overbrace{n = 1, 2, 3 \ldots}^{\text{quantum numbers}}$$

Quantized energy levels for a particle in a 1D box

$$E = \frac{m_l^2 h^2}{8 \pi^2 m r^2}$$

Quantized energies of a particle on a ring

$$\psi_{1s} = \frac{1}{\pi^{1/2} a_0^{3/2}} \mathrm{e}^{-r/a_0}$$

H-atom 1s wavefunction

$$\psi_{1s}^2 = \frac{1}{\pi a_0^3} \mathrm{e}^{-2r/a_0}$$

H-atom 1s probability density (per unit volume)

$$P(r) = 4 \pi r^2 \psi_{1s}^2 = \frac{4}{a_0^3} r^2 \mathrm{e}^{-2r/a_0}$$

H-atom 1s radial distribution function
(probability density per unit distance)

$$<r_{1s}> = \frac{4}{a_0^3} \int_{r=0}^{r=\infty} r^3 \mathrm{e}^{-2r/a_0} \, \mathrm{d} r$$

Average distance of a 1s H-atom electron from the nucleus

$$B(\bar{\nu}) = 2 \int_{\delta=0}^{\delta=\infty} I(\delta) \cos(2 \pi \bar{\nu} \delta) \, \mathrm{d} \delta$$

Fourier transform of an interferogram

$$\overbrace{F(\omega)}^{\text{normal spectrum}} = \sqrt{\frac{2}{\pi}} \int_{t=0}^{t=\infty} \overbrace{f(t)}^{\text{time domain}} \cos(\omega t) \, \mathrm{d} t$$

Fourier transform of a free induction decay

$$v = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d} t} = k [\mathrm{A}][\mathrm{B}]$$

Second-order rate law with two reactant species

$$\frac{c}{c_s} = 1 - \mathrm{e}^{-kt}$$

Dissolution of a solid as a function of time

$$q_r = \frac{8 \pi^2 I k_B T}{h^2}$$

Rotational partition function of a diatomic molecule

$$<r_{1s}> = \frac{3}{2} a_0$$

Average distance of a 1s electron in a H-atom

$$F(\omega) = \sqrt{\frac{2}{\pi}} \frac{a}{a^2 + \omega^2}$$

FT of the time domain signal exp($-at$)

$$\ln \frac{[\mathrm{A}]_0 \left([\mathrm{B}]_0 - x\right)}{[\mathrm{B}]_0 \left([\mathrm{A}]_0 - x\right)} = k \left([\mathrm{B}]_0 - [\mathrm{A}]_0\right) t$$

Integrated second-order rate law for two reactants

$$\Delta S(T_2 - T_1) = \int_{T_1}^{T_2} \frac{C_p}{T} \, \mathrm{d} T$$

Entropy from heat capacity and temperature data

$$f(c_x) = \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{1/2} \mathrm{e}^{-mc_x^2/2k_\mathrm{B}T}$$

$$f(c_x) = \left(\frac{M}{2\pi R T}\right)^{1/2} \mathrm{e}^{-Mc_x^2/2RT}$$

Maxwell-Boltzmann distribution in one-dimension

$$C_p = aT^3$$

Debye T-cubed law for temperatures near zero kelvin

$$<T_x> = \overbrace{\frac{1}{2}k_\mathrm{B}T}^{\textbf{per molecule}} = \overbrace{\frac{1}{2}RT}^{\textbf{per mole}}$$

Average kinetic energy in one-dimension

$$\int_a^b f(x)\,\mathrm{d}x \approx \sum_{k=1}^{N} (x_{k-1} - x_k)\frac{(y_{k-1} + y_k)}{2}$$

Trapezium rule for non-uniform trapezia

$$<y> = \frac{1}{n}\sum_{i=1}^{n} y_i$$

Average or mean value of a quantity

$$\sigma_y = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(y_i - <y>)^2} \qquad \sigma_y = \sqrt{\frac{1}{n-1}SSR}$$

Standard deviation of n data points

$$\sigma_y^2 = \left(\frac{\partial y}{\partial a}\right)^2 \sigma_a^2 + \left(\frac{\partial y}{\partial b}\right)^2 \sigma_b^2 + \left(\frac{\partial y}{\partial c}\right)^2 \sigma_c^2 + \ldots$$

Error propagation or variance equation

$$K_\mathrm{sp} = [\mathrm{Ag}^+(\mathrm{aq})][\mathrm{Cl}^-(\mathrm{aq})]$$

Solubility product or solubility constant of silver chloride

$$s = [\mathrm{Ag}^+(\mathrm{aq})\,\mathrm{mol\,L}^{-1}] = [\mathrm{Cl}^-(\mathrm{aq})\,\mathrm{mol\,L}^{-1}]$$

Solubility of Ag^+ or Cl^- in a saturated solution

$$E^\mathrm{T} = \frac{n^2h^2}{8mL^2}$$

Translational energy for a particle in a one-dimensional box

$$\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi l}{L}$$

Normalized wavefunction for a particle in a one-dimension box

$$\frac{N_i}{N} = \frac{\mathrm{e}^{-E_i/k_\mathrm{B}T}}{\sum_i \mathrm{e}^{-E_i/k_\mathrm{B}T}}$$

Boltzmann distribution of molecules in non-degerate energy levels

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

$$f(c) = 4\pi\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} c^2\mathrm{e}^{-mc^2/2k_\mathrm{B}T}$$

Maxwell-Boltzmann distribution in 3-D

$$c_\mathrm{mp} = \sqrt{\frac{2RT}{M}}$$

Most probable speed for the Maxwell-Boltzmann speed distribution

$$\frac{N_i}{N_j} = \mathrm{e}^{-(E_i - E_j)/k_\mathrm{B}T}$$

Ratio of the number of molecules in non-degenerate energy levels

$$\frac{N_u^{\mathrm{T}}}{N_g^{\mathrm{T}}} = \mathrm{e}^{-\left(4.918\times10^{-41}\,\mathrm{J}\right)/\left(1.381\times10^{-23}\,\mathrm{J\,K^{-1}}\right)\left(298\,\mathrm{K}\right)} = 1 \qquad \mathrm{H_2}\ \text{translational levels}$$

$$\frac{N_u^{\mathrm{R}}}{N_g^{\mathrm{R}}} = \mathrm{e}^{-\left(4.805\times10^{-21}\,\mathrm{J}\right)/\left(1.381\times10^{-23}\,\mathrm{J\,K^{-1}}\right)\left(298\,\mathrm{K}\right)} = 0.3111 \qquad \mathrm{H_2}\ \text{rotational levels}$$

$$\frac{N_u^{\mathrm{V}}}{n_g^{\mathrm{V}}} = \mathrm{e}^{-\left(8.2605\times10^{-20}\,\mathrm{J}\right)/\left(1.381\times10^{-23}\,\mathrm{J\,K^{-1}}\right)\left(298\,\mathrm{K}\right)} = 1.917\times10^{-9} \qquad \mathrm{H_2}\ \text{vibrational levels}$$