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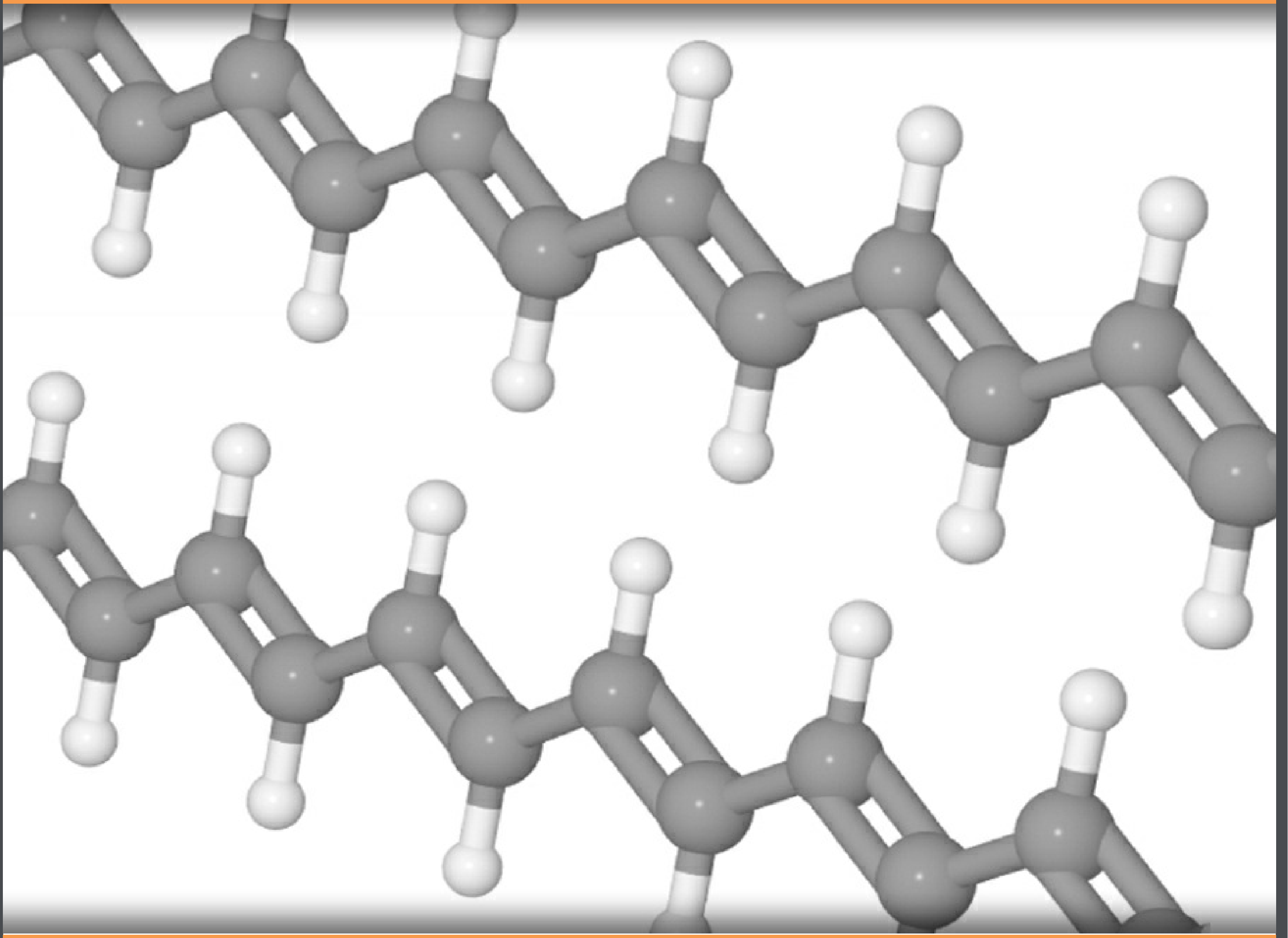
Intermediate Maths for Chemists

Chemistry Maths 2

J. E. Parker



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Contents

Acknowledgements

I was pleased to respond to Ventus Publishing to write a textbook (which is split into 3 more manageable books, “Chemistry Maths 1”, “Chemistry Maths 2”, and “Chemistry Maths 3” which should be studied in sequence) that would help Chemistry students survive, and even 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 the Chemistry Department, Heriot-Watt University, Edinburgh, Scotland. These tutorials have formed the basis for this workbook. I would like to thank the staff of Heriot-Watt University Chemistry Department for their help; and thank the students who for many years “suffered” these tutorials, I hope they helped them with their Chemistry 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 (year) of the degree you are studying. I hope you find this workbook helpful and I wish you good luck with your studies.

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Description of the Text

Chemistry Maths 2

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This text teaches Maths from a Chemistry perspective so that the student can see the relevance of Maths as the Language of Chemistry. It is the second part of a three part series of texts.

The text is aimed at first-year university undergraduates taking a degree in *Chemistry* or a Chemistry based subject such as *Chemical Engineering, Chemical Physics, Molecular Biology, Biochemistry* or *Biology.* The texts should also be useful to final year School or College students prior to their starting a university undergraduate degree. The material in Chemistry Maths 2 covers the last four teaching weeks of semester 1 and the first four weeks of semester 2 of a structured one-year Maths course for Chemists.

The text is made up of tutorial questions with fully worked solutions and is structured on a weekly basis to help the students to self-pace themselves. It contains many molecular structures and graphs in colour to illustrate both the Chemistry and the Maths. For ease of navigation there are page references between questions and their solutions (and back again) and also between the table of contents and the sections. These may be used in conjunction with the page viewer of your PDF reader.

List of Formulae

Chemistry Maths 2

J. E. Parker, Honorary Senior Lecturer, Heriot-Watt University.

The following are some of the Chemistry formulae encountered in this book.

Energy of a particle in a 2-dimensional box,

$$E_{n_1 n_2} = \frac{h^2}{8\,m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right)$$

Radial probability distribution for a H-atom 1*s* atomic orbital,

$$P = \frac{4}{a_0^3}\,r^2 \exp\left(-\frac{2\,r}{a_0}\right)$$

Consecutive first order reactions A → B → C,

$$[\mathrm{B}]_t = [\mathrm{A}]_0 \frac{k_\mathrm{a}}{k_\mathrm{b} - k_\mathrm{a}}\left(\exp\left(-k_\mathrm{a} t\right) - \exp\left(-k_\mathrm{b} t\right)\right)$$

$$[\mathrm{C}]_t = \frac{[\mathrm{A}]_0}{k_\mathrm{b} - k_\mathrm{a}}\left(k_\mathrm{b} - k_\mathrm{a} + k_\mathrm{a}\exp\left(-k_\mathrm{a} t\right) - k_\mathrm{b}\exp\left(-k_\mathrm{b} t\right)\right)$$

First-order kinetics $c\text{-}C_3H_6 \rightarrow CH_2CHCH_3$

$$k\,t = \ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x}$$

Rate of recombination of iodine atoms in the gas phase $I + I \rightarrow I_2$

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

Beer-Lamber Law,

$$\log\left(\frac{I}{I_0}\right) = -\,\varepsilon\,[\mathrm{A}]\,l$$

Fick's first law of diffusion and the average distance travelled by a molecule,

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -DA\frac{\mathrm{d}c}{\mathrm{d}x} \quad d = (2Dt)^{1/2}$$

Maxwell-Boltzmann speed distribution,

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

Schrödinger equation in one dimension,

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

Wavefunction for a particle in a 1-dimensional box,

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

Particle on a ring approximate treatment for the benzene π-electrons,

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

Spectroscopy and Fourier transform spectroscopy,

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

Second-order kinetics NO + $\mathrm{Cl_2}$ → NOCl + Cl

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

Hydrogen atom 1*s* atomic orbital radial wavefunction,

$$\psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{1/2}\exp\left(-\frac{r}{a_0}\right)$$

Entropy change and heat capacity,

$$\Delta S = \int_{S_1}^{S_2} \mathrm{d}S = \int_{T_1}^{T_2} \frac{C_p}{T}\, \mathrm{d}T$$

Average translational energy of a molecule in the *x* direction,

$$\bar{T}_x = \frac{1}{2} k_\mathrm{B} T$$

Lab experimental data and standard deviations,

$$\sigma_y = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left(y_i - \bar{y}\right)^2} \quad \text{or} \quad \sigma_y = \sqrt{\frac{1}{n-1}\, SSR}$$

Error propagation in experimental data calculations $y = f(a, b, c, \ldots)$

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

Statistical populations of quantum states (Boltzmann ratio),

$$\frac{n_i}{n_j} = \exp\left(-\frac{\varepsilon_i - \varepsilon_j}{k_\mathrm{B} T}\right)$$

Most probable speed of molecules,

$$v_\mathrm{mp} = \sqrt{\frac{2 k_\mathrm{B} T}{m}}$$

Introduction

Chemistry Maths 1, 2 and 3 are tutorial workbooks intended for first year undergraduates taking a degree in *Chemistry* or a Chemistry based subject such as *Chemical Engineering, Chemical Physics, Molecular Biology, Biochemistry* or *Biology.* The texts may also be very useful for final year school or college students prior to them starting an undergraduate degree. They are split into three in order to reduce file size and make handling on a laptop or tablet computer easier. Chemistry Maths 1 covers the first 8 weeks of semester 1; Chemistry Maths 2 the remainder of semester 1 and the beginning of semester 2; and Chemistry Maths 3 the rest of semester 2. They each have chapter heading such as Week 1, Week 2 and so on. This is purely to help you self-pace your work on a weekly basis although I realize that the week numbers in Chemistry Maths 2 and Chemistry Maths 3 will not correspond to your semester week numbers.

This workbook is *not* a textbook! Use your Chemistry and Maths textbook to find out the details about the area covered. People will not really understand something, including Maths, until they can use it in a flexible way. Tutorials are a way of allowing you to practice your skills, in this case the Maths required by Chemists, so that the Maths will become easier with practice.

I have deliberately repeated the introductory sections of Chemistry Maths 1 (Parker 2011) here for your convenience. Please also study Section 1.1.4 of Chemistry Maths 1 on Straight Line Graphs (Parker 2011). Several helpful textbooks for first year Chemists and their references are given at the end of this workbook.

Introduction: 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. Maths is also the underlying language of *all* Science, Engineering, Economics and many other subjects. So we won't be able to become fluent in Chemistry until we understand this "shorthand" language.

Introduction: How The Chemistry Maths 2 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 not the Chemistry, the Chemistry details will come later as you progress in your Chemistry 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 is otherwise a bit abstract.

Introduction: 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 in Maths. But in the sciences and engineering all the variables we use are *physical quantities*, such as mass, length, time, force, work, and so on. These physical quantities usually have a conventional symbol agreed by usage of the international community of scientists. 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, even if we may not be sure what it means, $E = mc^2$. 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 converting mass into energy. So this workbook 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.

$$\mathit{Physical\ Quantity} = (\text{pure number}) \times (\text{units})$$

Physical quantities consist of two parts, a pure number and a unit, which are inseparable. An example would be $c = 2.998\ \mathrm{m\ s^{-1}}$ where c is the symbol for the velocity of light. In order to clearly distinguish the physical quantity from its constituent parts, the physical quantity is written in *italics* and the pure number and the units are in roman (upright) font. Don't worry too much about hand written material but for typed material it should be done correctly.

For units named after people such as Sir Isaac Newton or Lord Kelvin, when referring to the person their name has an initial capital (Newton or Kelvin) but the unit is all lower case (newton or kelvin) and the symbol for the unit is initial capital (N or K). The use of initial capital for units has a few exception (for historical reasons) such the second (s) or the kilogram (kg).

When we substitute a physical quantity for its symbol into an equation we must substitute *both* the number *and* the units in the equation, they are inseparable, they go together like the two sides of a piece of paper.

As far as possible the workbook is organized on a weekly basis. Go through the examples and work out the solution yourself on paper then check the solution. A full solution is there for you to check that you are correct and to show the method of solving the problem. To begin with, the solutions give every single step 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.

Introduction: Suggested Textbooks (see page 101)

The Chemistry Maths 2 may be used with any Maths textbook, however, it is designed to interface with the textbook (Stroud and Booth 2007). Despite its name of *Engineering Mathematics* Stroud and Booth covers all the Maths needed by all the sciences and engineering subjects. Chemistry Maths 2 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 & Wille 2012) is excellent. In later years of your course then (Atkins & de Paula 2009) has many examples of the interplay between Chemistry and Maths mainly in the area of Physical Chemistry.

One final comment. A common mistake of Chemistry 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. There are a very *small* number of equations that become familiar by usage and which you remember without really having to try, all the rest come from being able to apply your Maths to this small number of equations (or to equations supplied in an exam or from a textbook) and this enables you to get to your target.

1 Week 1: Chemistry, Advanced Differentiation and the Maclaurin and Taylor Series

Advanced differentiation and the Maclaurin and Taylor series will take both Week 1 and Week 2. There are five Maths topics to be considered with respect to advanced differentiation and the tutorial questions reflect some of the most common uses that Chemistry makes of the five topics of advanced differentiation. These are the product rule, the quotient rule, the chain rule, parametric differentiation, and Maclaurin or Taylor 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. The Taylor series expansion for the function $f(a+x)$ is,

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

For $-x$ the expansion is as the following,

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

Note the alternation of sign for the even and odd powers of x. If that single point of the expansion is at $a = 0$ then the series is called a Maclaurin series. The Maclaurin series is shown below.

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

1.2 Week 1 Tutorial Questions

1.2.1 Question 1: Quantum Mechanics in Two Dimensions

Consider a particle, of mass m, in a two-dimensional box. This might be an electron confined in a quantum well on a semiconductor surface, for example, which is the Chemistry responsible for some solid state display devices. Fig. 1.1 shows the wavefunction of one of the many possible energy levels of an electron confined in such a situation.

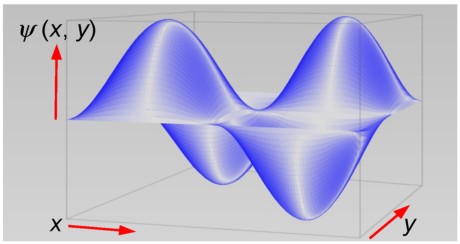


Figure 1.1: Wavefunction of the Allowed Energy Level $n_1 = 2, n_2 = 2, L_1 = 1, L_2 = 1$.

The energy levels $E_{n1,\,n2}$ for the particle depends on the lengths of the two sides of the box, L_1 and L_2, and the quantum numbers associated with these two directions are n_1 and n_2. The quantum numbers may each independently take the integer values 1, 2, 3, … that is $n_1 = 1, 2, 3.$ … and $n_2 = 1, 2, 3,$ …

$$E_{n_1 n_2} = \frac{h^2}{8m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right)$$

Keeping $E_{n1,n2}$ the energy of the particle constant, determine $\mathrm{d}L_1/\mathrm{d}L_2$ (where L_1 is an unknown function of L_2). This is an example of implicit differentiation, *i.e.* find $\mathrm{d}E_{n1,n2}/\mathrm{d}L_2$ and set this equal to zero as the energy is constant. The resulting expression may then be rearranged to find an equation for $\mathrm{d}L_1/\mathrm{d}L_2$.

Jump to Solution 1 (see page 16)

1.2.2 Question 2: Electrons in Atomic Orbitals

The probability of finding an electron at a given distance or radius, r, from the nucleus of an atom is given by the radial probability distribution, P. For the hydrogen atom in its lowest energy atomic orbital, 1*s*, the radial probability distribution function is given below.

$$P = \frac{4}{a_0^3} r^2 \exp\left(-\frac{2r}{a_0}\right)$$

Where a_0 is a constant called the Bohr radius.

What is the most probable radius at which to find the electron? In order to find the maximum value of P we need to find the differential dP/dr using the product rule and set this equal to zero.

Jump to Solution 2 (see page 18)

1.2.3 Question 3: Vibration of Molecular Bonds and Heat Capacity

The contribution to the total energy of n moles of diatomic molecules arising from their molecular vibrations is given by the equation,

$$E = nN_A hc\nu \frac{\exp(-hc\nu\beta)}{1-\exp(-hc\nu\beta)}$$

Where n, N_A, h, c, ν are all constants for n moles of a given molecule. $\beta = 1/k_B T$ with k_B = Boltzmann's constant ($k_B = R/N_A$); R is the gas constant, T is the absolute temperature; ν is the vibrational frequency of the chemical bond; N_A is Avogadro's constant; h is Planck's constant; and c is the velocity of light.

Find an equation for the heat capacity of the collection of molecules at constant volume, C_V, by substituting for the differential dE/dβ in the equation below.

$$C_V = -k_B\beta^2 \frac{dE}{d\beta}$$

The differentiation dE/dβ will require the quotient rule. Then at the *final* stage substitute for $\beta = 1/k_B T$ and then $k_B = R/N_A$.

Jump to Solution 3 (see page 21)

1.3 Week 1 Tutorial Solutions

1.3.1 Solution 1: Quantum Mechanics in Two Dimensions

$$E_{n_1 n_2} = \frac{h^2}{8m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right)$$

Using implicit differentiation, we differentiate the energy $E_{n1,\,n2}$ with respect to the distance L_2 because the question asks for dL_1/dL_2 with dL_2 as the denominator. Note that $h^2/8m$ is a constant which can be taken outside the differential.

$$\frac{dE_{n_1 n_2}}{dL_2} = \frac{h^2}{8m}\frac{d}{dL_2}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right)$$

Expanding the brackets gives two terms.

$$\frac{\mathrm{d}\,E_{n_1\,n_2}}{\mathrm{d}\,L_2} = \frac{h^2}{8\,m}\left(\frac{\mathrm{d}}{\mathrm{d}\,L_2}\left(\frac{n_1^2}{L_1^2}\right)+\frac{\mathrm{d}}{\mathrm{d}\,L_2}\left(\frac{n_2^2}{L_2^2}\right)\right)$$

The second term in the bracket is easy as the variable is L_2 and the differentiation is by L_2. Differentiating the second term gives,

$$\frac{\mathrm{d}}{\mathrm{d}\,L_2}\left(\frac{n_2^2}{L_2^2}\right) = n_2^2\,\frac{\mathrm{d}\,L_2^{-2}}{\mathrm{d}\,L_2} = n_2^2\left(-2\,L_2^{-3}\right) = -\frac{2\,n_2^2}{L_2^3}$$

Substituting for the second term in the $\mathrm{d}E_{n1,\,n2}/\mathrm{d}L_2$ equation gives,

$$\frac{\mathrm{d}\,E_{n_1\,n_2}}{\mathrm{d}\,L_2} = \frac{h^2}{8\,m}\left(\frac{\mathrm{d}}{\mathrm{d}\,L_2}\left(\frac{n_1^2}{L_1^2}\right) - \frac{2\,n_2^2}{L_2^3}\right)$$

For the first term in the brackets the variable is L_1 and the differentiation is by L_2 hence we need to use the chain rule,

$$\frac{\mathrm{d}\,y}{\mathrm{d}\,L_2} = \frac{\mathrm{d}\,y}{\mathrm{d}\,L_1}\,\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2}$$

Applying the chain rule to the $\mathrm{d}E_{\mathrm{n1\,n2}}/\mathrm{d}L_2$ equation gives,

$$\frac{\mathrm{d}\,E_{n_1\,n_2}}{\mathrm{d}\,L_2} = \frac{h^2}{8\,m}\left(\frac{\mathrm{d}}{\mathrm{d}\,L_1}\left(\frac{n_1^2}{L_1^2}\right)\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} - \frac{2\,n_2^2}{L_2^3}\right)$$

The first term in the brackets becomes,

$$\frac{\mathrm{d}}{\mathrm{d}\,L_1}\left(\frac{n_1^2}{L_1^2}\right)\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} = n_1^2\,\frac{\mathrm{d}\,L_1^{-2}}{\mathrm{d}\,L_1}\,\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} = n_1^2\left(-\,2\,L_1^{-3}\right)\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} = -\,\frac{2\,n_1^2}{L_1^3}\,\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2}$$

Substituting the first term in the $\mathrm{d}E_{\mathrm{n1,\,n2}}/\mathrm{d}L_2$ equation gives the overall differential as,

$$\frac{\mathrm{d}\,E_{n_1\,n_2}}{\mathrm{d}\,L_2} = \frac{h^2}{8\,m}\left(-\,\frac{2\,n_1^2}{L_1^3}\,\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} - \frac{2\,n_2^2}{L_2^3}\right)$$

Remembering from the question that the energy $E_{\mathrm{n1,\,n2}}$ is constant, then $\mathrm{d}E_{\mathrm{n1,\,n2}}/\mathrm{d}L_2 = 0$ and so,

$$0 = \frac{h^2}{8\,m}\left(-\,\frac{2\,n_1^2}{L_1^3}\,\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} - \frac{2\,n_2^2}{L_2^3}\right)$$

Either $h^2/8m$ equals zero or the terms in the bracket equals zero. As $h^2/8m$ cannot be equal to zero, then the bracketed expression must equal zero. The question wanted $\mathrm{d}L_1/\mathrm{d}L_2$ derived,

$$0 = \left(-\,\frac{2\,n_1^2}{L_1^3}\,\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} - \frac{2\,n_2^2}{L_2^3}\right) \qquad \frac{2\,n_1^2}{L_1^3}\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} = -\,\frac{2\,n_2^2}{L_2^3} \qquad \frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} = -\,\frac{2\,n_2^2}{L_2^3}\,\frac{L_1^3}{2\,n_1^2}$$

Which if we write more tidily becomes.

$$\boxed{\frac{\mathrm{d}\,L_1}{\mathrm{d}\,L_2} = -\left(\frac{n_2}{n_1}\right)^2\left(\frac{L_1}{L_2}\right)^3}$$

So staying in the same quantum energy level at the same total energy but changing the length of one side of the *two-dimensional* “box” requires us to change the length of the other side in the *cube* of the ratio of the lengths.

Return to Question 1 (see page 15)

1.3.2 Solution 2: Electrons in Atomic Orbitals

$$P = \frac{4}{a_0^3}\,r^2\,\exp\left(-\,\frac{2\,r}{a_0}\right)$$

Differentiate the radial probability distribution with respect to *r* using the product rule.

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

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

$$\frac{\mathrm{d}P}{\mathrm{d}r} = -\frac{8}{a_0^4}\, r^2 \exp\left(-\frac{2r}{a_0}\right) + \frac{8}{a_0^3}\, r\exp\left(-\frac{2r}{a_0}\right)$$

Which writing the positive term first is,

$$\frac{\mathrm{d}P}{\mathrm{d}r} = \frac{8}{a_0^3}\, r\exp\left(-\frac{2r}{a_0}\right) - \frac{8}{a_0^4}\, r^2 \exp\left(-\frac{2r}{a_0}\right)$$

and then taking out any common factors outside a brackets gives,

$$\frac{\mathrm{d}P}{\mathrm{d}r} = \frac{8}{a_0^3}\, r\exp\left(-\frac{2r}{a_0}\right)\left(1-\frac{r}{a_0}\right)$$

To find the maximum probability, we set the derivative to zero, and then exam the three terms involving *r* to find the one value of *r* that gives the maximum in *P*.

$$0 = \frac{8}{a_0^3}\, r\exp\left(-\frac{2r}{a_0}\right)\left(1-\frac{r}{a_0}\right)$$

The derivative is equal to zero if any of the three terms involving *r* are equal to zero *i.e.* $(8r/a_0^3) = 0$; or $\exp(-2r/a_0) = 0$; or $(1 - r/a_0) = 0$.

The first term, $(8r/a_0^3)$, is zero at $r = 0$.

Looking at the exponential term the radial distance of the electron from the nucleus is always positive and so $-2r/a_0$ is always negative. Fig. 1.2 shows the shape of a general negative exponential function and the exponential term is zero $\exp(-2r/a_0) = 0$ at $r = \infty$.

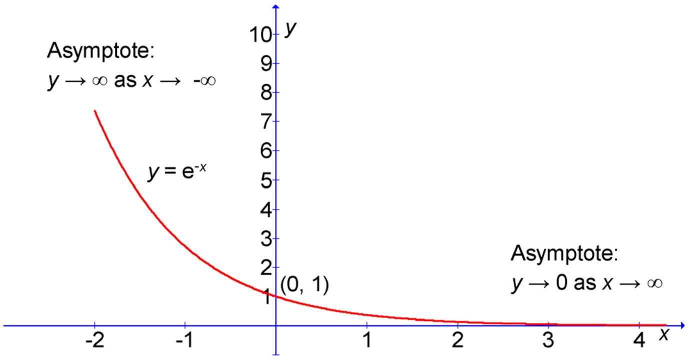


Figure 1.2: A Negative Exponential Function.

For the three terms the derivative is zero at $r = 0$, $r = \infty$, and $(1 - r/a_0) = 0$, respectively. Also the probability distribution function P is zero at $r = 0$ and $r = \infty$ thus the maximum must be when the $(1 - r/a_0) = 0$. Which gives the maximum in the radial probability function at $r = a_0$ the Bohr radius.

$$P_{\max} \text{ is at } r = a_0 = 0.5292 \times 10^{-10} \text{ m}$$

Fig 1.3 shows the radial distribution function for the hydrogen 1*s* atomic orbital plotted using $a_0 = 0.5292$ Å.

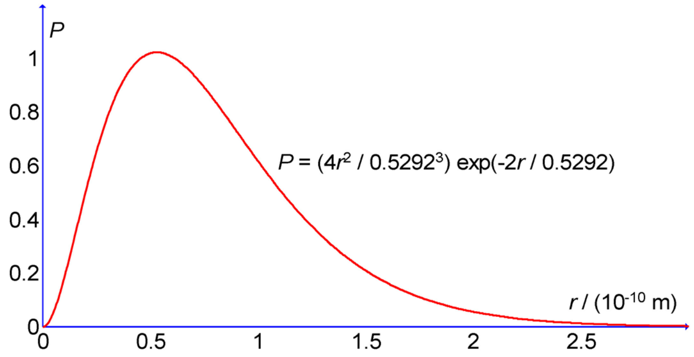


Figure 1.3: Hydrogen Atom 1s Radial Distribution Function.

The 1*s* radial probability distribution depends upon the radius *r* but *not* upon the values of *x*, *y*, or *z*.

$$P = \frac{4}{a_0^3} r^2 \exp\left(-\frac{2r}{a_0}\right)$$

Thus in Chemistry we may show the 1*s* atomic orbital as a sphere with the centre at the nucleus and the surface may be drawn at $r = a_0$ the maximum as in Fig. 1.4 or any other multiple of a_0. The probability is still very significant beyond this "surface" distance as shown in Fig. 1.3 and indeed asymptotically extends out to $r = \infty$ as we have shown.

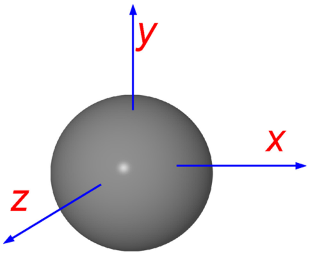


Figure 1.4: Hydrogen Atom 1s Atomic Orbital Drawn as a Sphere of Radius $r = a_0$.

Return to Question 2 (see page 15)

1.3.3 Solution 3: Vibration of Molecular Bonds and Heat Capacity

$$E = n N_A h c \nu \frac{\exp(-hc\nu\beta)}{1 - \exp(-hc\nu\beta)}$$

The heat capacity at constant volume is given by,

$$C_V = -k_B \beta^2 \frac{dE}{d\beta}$$

Substituting for the energy E we have,

$$C_V = -k_B \beta^2 \frac{d}{d\beta}\left(n N_A h c \nu \frac{\exp(-hc\nu\beta)}{1-\exp(-hc\nu\beta)}\right)$$

Taking the constants $nN_A hc\nu$ outside the differential gives,

$$C_V = -nN_A hc\nu\, k_B \beta^2 \frac{d}{d\beta}\left(\frac{\exp(-hc\nu\beta)}{1-\exp(-hc\nu\beta)}\right)$$

Concentrating just for the moment on the differential term of this intermediate result, we see it requires the quotient rule.

$$\frac{d}{d\beta}\left(\frac{y}{z}\right) = \frac{z\left(\frac{dy}{d\beta}\right) - y\left(\frac{dz}{d\beta}\right)}{z^2}$$

We have the following for y and z.

$$y = \exp(-hc\nu\beta) \qquad \frac{dy}{d\beta} = -hc\nu \exp(-hc\nu\beta)$$

$$z = 1-\exp(-hc\nu\beta) \qquad \frac{dz}{d\beta} = +hc\nu \exp(-hc\nu\beta)$$

Using the quotient rule on the differential term of the heat capacity gives,

$$\frac{d}{d\beta}\frac{\exp(-hc\nu\beta)}{1-\exp(-hc\nu\beta)} = \frac{(1-\exp(-hc\nu\beta))(-hc\nu\exp(-hc\nu\beta)) - (\exp(-hc\nu\beta))hc\nu\exp(-hc\nu\beta))}{(1-\exp(-hc\nu\beta))^2}$$

This looks frightening, *don't panic*, we will multiply out the brackets and remember that $(e^{-x})(e^{-x}) = e^{-2x}$.

$$\frac{d}{d\beta}\frac{\exp(-hc\nu\beta)}{1-\exp(-hc\nu\beta)} = \frac{-hc\nu\exp(-hc\nu\beta) + hc\nu\exp(-2hc\nu\beta) - hc\nu\exp(-2hc\nu\beta)}{(1-\exp(-hc\nu\beta))^2}$$

The second and third terms in the numerator cancel one another out.

$$\frac{\mathrm{d}}{\mathrm{d}\beta}\,\frac{\exp(-hc\nu\beta)}{1-\exp(-hc\nu\beta)}=\frac{-hc\nu\,\exp(-hc\nu\beta)}{\left(1-\exp(-hc\nu\beta)\right)^2}$$

The heat capacity equation can now be evaluated by substituting this into the intermediate result highlighted in yellow.

$$C_V=-nN_\mathrm{A}hc\nu\,k_\mathrm{B}\beta^2\,\frac{-hc\nu\,\exp(-hc\nu\beta)}{\left(1-\exp(-hc\nu\beta)\right)^2}$$

$$C_V=+nN_\mathrm{A}k_\mathrm{B}h^2c^2\nu^2\beta^2\,\frac{\exp(-hc\nu\beta)}{\left(1-\exp(-hc\nu\beta)\right)^2}$$

This is complete but we can clean up the equation using $k_\mathrm{B} = R/N_\mathrm{A}$ and $\beta = 1/k_\mathrm{B}T$.

$$C_V=nR\left(\frac{hc\nu}{k_\mathrm{B}T}\right)^2\frac{\exp(-hc\nu/k_\mathrm{B}T)}{\left(1-\exp(-hc\nu/k_\mathrm{B}T)\right)^2}$$

Return to Question 3 (see page 16)

2 Week 2: Chemistry, Advanced Differentiation and the Maclaurin and Taylor Series

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 also decays. Consecutive chemical reactions are also very common in organic, inorganic and biochemical reactions. An example is the reaction of *t*-butyl bromide (tertiary-butyl bromide or 2-bromo-2-methylpropane) dissolved in water containing a small concentration of sodium hydroxide. In Chemistry this reaction is an example of an S_N1 reaction. The first slow reaction is the loss of bromide ion Br^- from the *t*-butyl bromide to form a *t*-butyl carbocation. Figs 2.1 shows the structures of *t*-butyl bromide, the *t*-butyl carbocation.

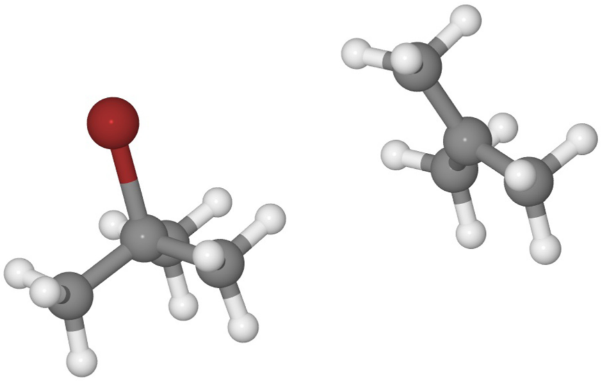


Figure 2.1: *t*-Butyl Bromide and *t*-Butyl Carbocation Structures.
C = dark grey, H = grey, Br = dark red.

The faster second reaction is the covalent bond formation between a hydroxide ion and a *t*-butyl carbocation to form the product molecule, a tertiary alcohol, *t*-butanol.

$$\left(CH_3\right)_3C^+ + OH^- \rightarrow \left(CH_3\right)_3C-OH$$

Fig 2.2 shows the structure of *t*-butanol.

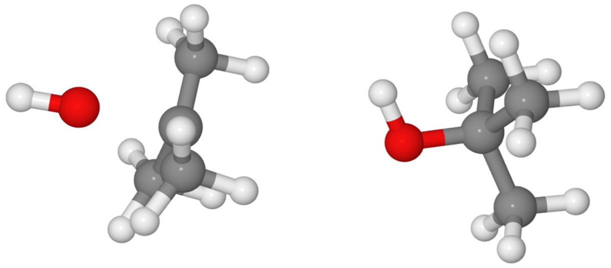


Figure 2.2: Hydroxide Ion, *t*-Butyl Carbocation and *t*-Butanol Structures.
C = dark grey, H = grey, O = red.

For the consecutive first-order reactions,

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

The rate constants for the reaction A to B is k_a and for the reaction B to C is k_b. At any given time, t, the concentrations of B and C can be expressed as follows in terms of the initial concentration of A, $[\mathrm{A}]_0$ as,

$$[\mathrm{B}]_t = [\mathrm{A}]_0 \frac{k_\mathrm{a}}{k_\mathrm{b} - k_\mathrm{a}} \left(\exp\left(-k_\mathrm{a} t\right) - \exp\left(-k_\mathrm{b} t\right)\right)$$

$$[\mathrm{C}]_t = \frac{[\mathrm{A}]_0}{k_\mathrm{b} - k_\mathrm{a}} \left(k_\mathrm{b} - k_\mathrm{a} + k_\mathrm{a} \exp\left(-k_\mathrm{a} t\right) - k_\mathrm{b} \exp\left(-k_\mathrm{b} t\right)\right)$$

Firstly, determine $\mathrm{d}[\mathrm{C}]_\mathrm{t} / \mathrm{d}[\mathrm{B}]_\mathrm{t}$ this is a parametric differentiation using the chain rule. Secondly, what does $\mathrm{d}[\mathrm{C}]_\mathrm{t} / \mathrm{d}[\mathrm{B}]_\mathrm{t}$ *approximately* equal when $k_\mathrm{b} \gg k_\mathrm{a}$ *i.e.* a slow first reaction followed by a fast second reaction.

Jump to Solution 1 (see page 27)

2.1.2 Question 2: Vibrational Energy for a Collection of Molecules

All molecules are vibrating all the time, even at zero kelvin, their bonds are never "stationary" (this is due to Heisenberg's Uncertainty Principle). The bond distance of a vibrating diatomic molecule oscillates between a minimum value and a maximum value. The resistance of the bond to stretching is the force constant k, and the displacement from the equilibrium distance, r_e, is $(r - r_\mathrm{e})$. The vibrations may be treated rather like a mechanical spring and the potential energy, V, due to the vibration of the bond is $V = ½k(r - r_\mathrm{e})^2$ as shown as the red parabola in Fig. 2.3. Treating the vibrating bond like a mechanical spring is called the *harmonic oscillator* approximation and the vibrational quantum number, v, may take the values $v = 0, 1, 2, 3, \ldots$

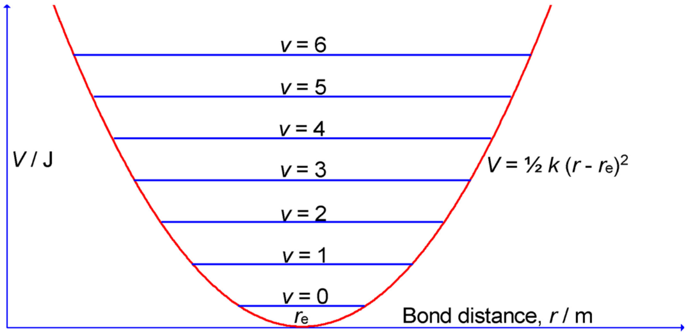


Figure 2.3: The Allowed Vibrational Quantum Levels of a Harmonic Oscillator Molecule.

Consider the total vibrational energy, E, of n moles of diatomic molecules (mentioned in section 1.2.3).

$$E = nN_A hc\nu \frac{\exp(-hc\nu\beta)}{1 - \exp(-hc\nu\beta)}$$

Where $\beta = 1/k_B T$ with (k_B = Boltzmann's constant which is the gas constant per *molecule* and T is the absolute temperature); ν is the vibrational frequency; and N_A is Avogadro's constant; h is Planck's constant; and c is the velocity of light.

Use a Maclaurin series expansion of $\exp(-hc\nu\beta)$ to show that when the temperature is high (and thus $hc\nu\beta \ll 1$) that the vibrational energy becomes, $E \approx nRT$.

Jump to Solution 2 (see page 30)

2.1.3 Question 3: Chemical Reaction with First-Order Kinetics

An example of a first order reaction is the isomerization from c-propane to propene which occurs at around 500°C. The structures of the two isomers are shown in Fig. 2.4.

$$c\text{-C}_3\text{H}_6 \rightarrow \text{CH}_2\text{CHCH}_3$$

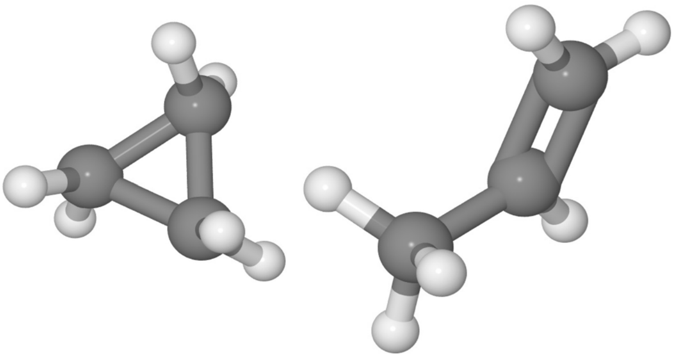


Figure 2.4: Cyclopropane and Propene. C = grey and H = light grey.

The integrated rate equation for a first-order reaction is,

$$k\,t = \ln \frac{[\text{A}]_0}{[\text{A}]_0 - x}$$

Where k is the rate constant; $[\text{A}]_0$ the original concentration of reactant (c-propane in this case); and x is the concentration of A that has been *lost* through reaction at a time t.

Expand $\ln([\text{A}]_0 - x)$ using a Taylor series, and show that when $[\text{A}]_0$ » x (*i.e.* early in the reaction) the rate of reaction is linear in x.

Jump to Solution 3 (see page 31)

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.

$$[\text{B}]_t = [\text{A}]_0 \frac{k_\text{a}}{k_\text{b} - k_\text{a}} \left(\exp(-k_\text{a} t) - \exp(-k_\text{b} t)\right)$$

$$[\text{C}]_t = \frac{[\text{A}]_0}{k_\text{b} - k_\text{a}} \left(k_\text{b} - k_\text{a} + k_\text{a}\exp(-k_\text{a} t) - k_\text{b}\exp(-k_\text{b} t)\right)$$

This is an example of parametric differentiation using the chain rule.

$$\frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}[\mathrm{B}]_t}\frac{\mathrm{d}[\mathrm{B}]_t}{\mathrm{d}t}$$

Rearranging the chain rule to give the required derivative.

$$\frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}[\mathrm{B}]_t} = \frac{\dfrac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}t}}{\dfrac{\mathrm{d}[\mathrm{B}]_t}{\mathrm{d}t}}$$

Firstly, find the derivative of $[\mathrm{C}]_t$ with respect to time.

$$\frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{[\mathrm{A}]_0}{k_\mathrm{b} - k_\mathrm{a}}\left(k_\mathrm{b} - k_\mathrm{a} + k_\mathrm{a}\exp(-k_\mathrm{a}t) - k_\mathrm{b}\exp(-k_\mathrm{b}t)\right)\right)$$

Moving the constant $[\mathrm{A}]_0/(k_\mathrm{b} - k_\mathrm{a})$ outside the derivative,

$$\frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}t} = \frac{[\mathrm{A}]_0}{k_\mathrm{b} - k_\mathrm{a}}\frac{\mathrm{d}}{\mathrm{d}t}\left(k_\mathrm{b} - k_\mathrm{a} + k_\mathrm{a}\exp(-k_\mathrm{a}t) - k_\mathrm{b}\exp(-k_\mathrm{b}t)\right)$$

$$\frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}t} = \frac{[\mathrm{A}]_0}{k_\mathrm{b} - k_\mathrm{a}}\left(0 - 0 - k_\mathrm{a}^2\exp(-k_\mathrm{a}t) + k_\mathrm{b}^2\exp(-k_\mathrm{b}t)\right)$$

$$\frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}t} = \frac{[\mathrm{A}]_0}{k_\mathrm{b} - k_\mathrm{a}}\left(-k_\mathrm{a}^2\exp(-k_\mathrm{a}t) + k_\mathrm{b}^2\exp(-k_\mathrm{b}t)\right)$$

The derivative of $[\mathrm{B}]_t$ with respect to time is also required.

$$\frac{\mathrm{d}[\mathrm{B}]_t}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left([\mathrm{A}]_0\frac{k_\mathrm{a}}{k_\mathrm{b} - k_\mathrm{a}}\left(\exp(-k_\mathrm{a}t) - \exp(-k_\mathrm{b}t)\right)\right)$$

Taking the constants outside the derivative.

$$\frac{\mathrm{d}[\mathrm{B}]_t}{\mathrm{d}t} = [\mathrm{A}]_0\frac{k_\mathrm{a}}{k_\mathrm{b} - k_\mathrm{a}}\frac{\mathrm{d}}{\mathrm{d}t}\left(\exp(-k_\mathrm{a}t) - \exp(-k_\mathrm{b}t)\right)$$

$$\frac{\mathrm{d}[\mathrm{B}]_t}{\mathrm{d}t} = [\mathrm{A}]_0\frac{k_\mathrm{a}}{k_\mathrm{b} - k_\mathrm{a}}\left(-k_\mathrm{a}\exp(-k_\mathrm{a}t) + k_\mathrm{b}\exp(-k_\mathrm{b}t)\right)$$

Substituting these two derivatives into $\mathrm{d}[\mathrm{C}]_t/\mathrm{d}[\mathrm{B}]_t$ gives,

$$\frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}[\mathrm{B}]_t} = \frac{\frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}t}}{\frac{\mathrm{d}[\mathrm{B}]_t}{\mathrm{d}t}} = \frac{\frac{[\mathrm{A}]_0}{k_\mathrm{b}-k_\mathrm{a}}\left(-k_\mathrm{a}^2\exp(-k_\mathrm{a}t)+k_\mathrm{b}^2\exp(-k_\mathrm{b}t)\right)}{[\mathrm{A}]_0\frac{k_\mathrm{a}}{k_\mathrm{b}-k_\mathrm{a}}\left(-k_\mathrm{a}\exp(-k_\mathrm{a}t)+k_\mathrm{b}\exp(-k_\mathrm{b}t)\right)}$$

$$\frac{\mathrm{d}[\mathrm{C}]_t}{\mathrm{d}[\mathrm{B}]_t} = \frac{1}{k_\mathrm{a}}\,\frac{-k_\mathrm{a}^2\exp(-k_\mathrm{a}t)+k_\mathrm{b}^2\exp(-k_\mathrm{b}t)}{-k_\mathrm{a}\exp(-k_\mathrm{a}t)+k_\mathrm{b}\exp(-k_\mathrm{b}t)}$$

This is the *general* solution which is true under *all* conditions. Fig. 2.5 shows the shape of a negative exponential function.

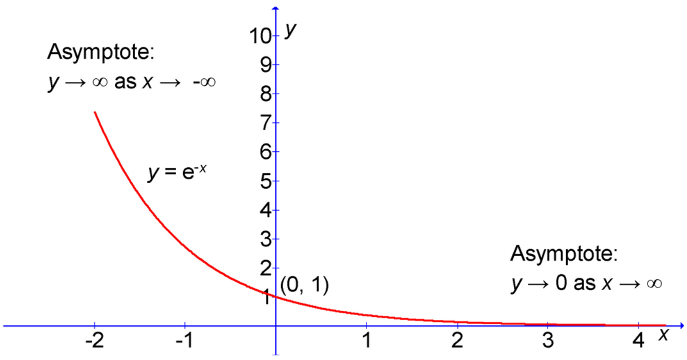
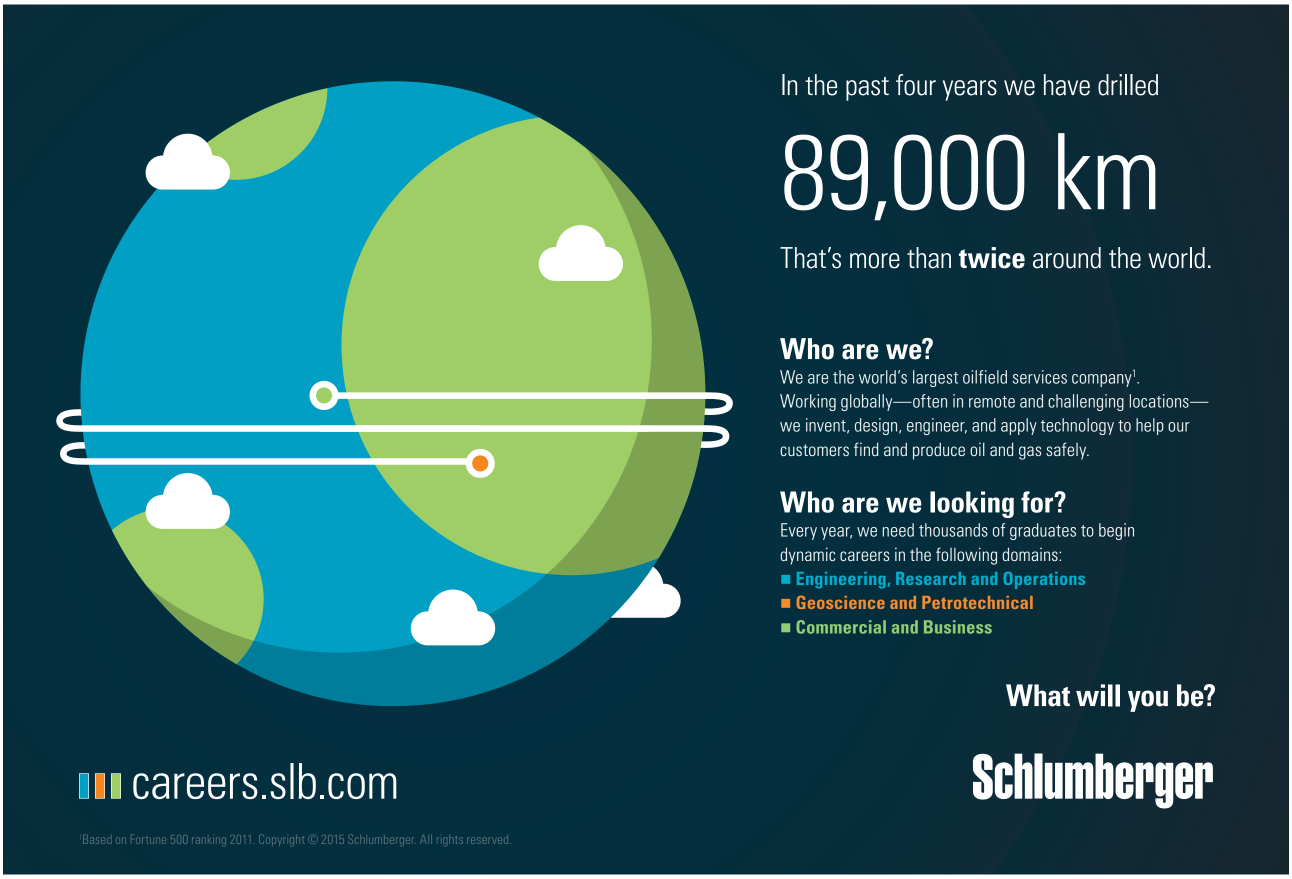


Figure 2.5: The Shape of a Negative Exponential Curve.



If $k_b \gg k_a$ then from Fig. 2.5 $\exp(-k_b t) \ll \exp(-k_a t)$, that is terms involving $\exp(-k_a t)$ are dominant whilst those involving $\exp(-k_b t)$ are negligible. We can approximate the denominator and numerator where they involve addition or subtraction of such terms. So the above general solution approximates to,

$$\frac{\mathrm{d}\,[\mathrm{C}]_t}{\mathrm{d}\,[\mathrm{B}]_t} = \frac{1}{k_\mathrm{a}} \frac{-k_\mathrm{a}^2 \exp(-k_\mathrm{a} t) + k_\mathrm{b}^2 \exp(-k_\mathrm{b} t)}{-k_\mathrm{a} \exp(-k_\mathrm{a} t) + k_\mathrm{b} \exp(-k_\mathrm{b} t)} \approx \frac{1}{k_\mathrm{a}} \frac{-k_\mathrm{a}^2 \exp(-k_\mathrm{a} t)}{-k_\mathrm{a} \exp(-k_\mathrm{a} t)} \approx 1$$

$$\frac{\mathrm{d}\,[\mathrm{C}]_t}{\mathrm{d}\,[\mathrm{B}]_t} \approx 1$$

This is consistent with the first *slow* reaction being the *rate determining step* ($k_b \gg k_a$), the first step in the consecutive sequence is the chemical “bottleneck” which determines the overall speed. Thus the concentrations of the final product [C] and the intermediate molecule [B] changes at the same rate. For the S_N1 reaction of *t*-butyl bromide the first slow reaction, the loss of Br^-, is the rate determining step.

Return to Question 1 (see page 24)

2.2.2 Solution 2: Vibrational Energy for a Collection of Molecules

Use a Maclaurin series expansion of $\exp(-hc\nu\beta)$ and then approximate the series for when the temperature is high (that is β is small) and thus when $hc\nu\beta \ll 1$.

$$\frac{\mathrm{d}}{\mathrm{d}\,x} f(x) = \frac{\mathrm{d}}{\mathrm{d}\,\beta} \exp(-hc\nu\beta) = -hc\nu \exp(-hc\nu\beta) \qquad \frac{\mathrm{d}}{\mathrm{d}\,x} f(0) = -hc\nu$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\,x^2} f(x) = h^2c^2\nu^2 \exp(-hc\nu\beta) \qquad \frac{\mathrm{d}^2}{\mathrm{d}\,x^2} f(0) = h^2c^2\nu^2$$

$$\frac{\mathrm{d}^3}{\mathrm{d}\,x^3} f(x) = -h^3c^3\nu^3 \exp(-hc\nu\beta) \qquad \frac{\mathrm{d}^3}{\mathrm{d}\,x^3} f(0) = -h^3c^3\nu^3$$

Note the alternation of signs for even and odd powers. These derivatives may now be substituted into the Maclaurin series to give the approximation of $f(x)$ at $f(0)$.

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

$$\exp(-hc\nu\beta) = 1 + \beta(-hc\nu) + \frac{\beta^2}{2}(h^2c^2\nu^2) + \frac{\beta^3}{6}(-h^3c^3\nu^3) + \ldots$$

If β is small we can drop the squared and higher powered terms in β,

$$\exp(-hc\nu\beta) \approx 1 - hc\nu\beta$$

Substitute this into the expression for the energy.

$$E = nN_A hc\nu \frac{\exp(-hc\nu\beta)}{1-\exp(-hc\nu\beta)} \qquad E \approx nN_A hc\nu \frac{1-hc\nu\beta}{1-(1-hc\nu\beta)}$$

$$E \approx nN_A hc\nu \frac{1-hc\nu\beta}{hc\nu\beta} \qquad E \approx \frac{nN_A}{\beta}(1-hc\nu\beta)$$

We use $hc\nu\beta \ll 1$, because β is small, to simplify the term in brackets and then substitute $\beta = 1/k_B T$.

$$E \approx \frac{nN_A}{\beta} \approx nN_A k_B T$$

The Boltzmann constant is the gas constant per molecule $k_B = R/N_A$ that is $R = k_B N_A$.

$$E \approx nRT$$

This result is an example of the *equipartition theorem*, a simple rule for determining the approximate energy of a system that is used in chemical thermodynamics, but which is only approximately true at *high* temperatures and which will be covered later in your Chemistry lectures.

Return to Question 2 (see page 25)

2.2.3 Solution 3: Chemical Reaction with First Order Kinetics

$$kt = \ln \frac{[A]_0}{[A]_0 - x}$$

Rearranging the logarithm in the rate equation for the isomerization reaction.

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

Expanding the $\ln([A]_0 - x)$ term in a Taylor series.

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

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

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

Substituting the Taylor series expanded equation for the $\ln([A]_0 - x)$ term into the integrated rate equation, gives,

$$k\,t = \ln[A]_0 - \left(\ln[A]_0 - \frac{x}{[A]_0} - \frac{x^2}{2[A]_0^2} - \frac{x^3}{3[A]_0^3} + \ldots\right)$$

$$k\,t = \frac{x}{[A]_0} + \frac{x^2}{2[A]_0^2} + \frac{x^3}{3[A]_0^3} + \ldots$$

Early on at the beginning of the reaction $[A]_0 \gg x$ and the squared and the higher order terms can be neglected because we are dividing a small concentration, x, by a very large concentration, $[A]_0$, which gives an extremely small ratio for these higher order terms.

$$k\,t \approx \frac{x}{[A]_0}$$

The rate of reaction, v, for a first-order reaction is

$$v = k[A]_0 \approx \frac{x}{t}$$

Initially (at very small times) the rate of reaction, v, for a first-order reaction is directly proportional to x.

$$\boxed{v \approx \frac{x}{t}}$$

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. Some general example are,

$$a\frac{\mathrm{d}y}{\mathrm{d}x} + by + c = 0 \qquad a\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + b\frac{\mathrm{d}y}{\mathrm{d}x} + cy + d = 0 \qquad a\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + by + c = 0$$

Where a, b, c and d are constants. ODE represent *dynamic* situations, that is where quantities are changing and such situations are very common in Chemistry and chemically based science and engineering. A simple example of an ODE is Newton's Second Law of Motion that the force at a certain time, $F(t)$, equals mass times acceleration.

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = F(t)$$

The word *ordinary* is to distinguish them from *partial* differential equations, where the dependent variable, y, is a function of more than one independent variables, x, z, etc.

3.1.1 First-Order Ordinary Differential Equations

$$a\frac{\mathrm{d}y}{\mathrm{d}x} + by = f(x, y)$$

This type of ODE 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 one of the following both of which are first-order ODEs. First-order ODEs are common in chemical kinetics where we are measuring the speed or rate of an event (*e.g.* the rate of chemical reaction, and the rate of diffusion).

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]^2 \qquad \text{or} \qquad \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}]$$

If the first-order ODE can be rearranged to be in the form below it can be solved by direct integration (see Parker 2011, Week 7 and Week 8).

$$\frac{\mathrm{d}y}{\mathrm{d}x} = f(x) \qquad \int \mathrm{d}y = \int f(x)\,\mathrm{d}x$$

One the other hand, if the first-order ODE can only be rearranged to be in the form below it can be solved by the separation of the variables method (see Parker 2011, Section 7.2.1).

$$\frac{\mathrm{d}\,y}{\mathrm{d}\,x} = f(x\,,y)$$

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 $[\mathrm{A}]_0$ at time equals zero, $t = 0$. The Maths of first-order differential equations is also used to locate the turning points (maxima, minima, and points of inflexion) of plots of physical data. First-order ODE tutorial questions will be covered in Week 3.

3.1.2 Second-Order Ordinary Differential Equations

In Chemistry the other type of ODE that commonly occurs is the second-order ODE. A second-order ODE involved the *second* derivative as the highest derivative, such as

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

Where a, b, c, d are constants. In Chemistry second-order ODEs are common in quantum mechanics (also called wave mechanics). The Schrödinger equation describes the wavefunctions for a particle of mass m. For instance if the particle is moving in one-dimension, x, then,

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

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) and h is Planck's constant..

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 x. We will solve some simple second-order differential equations (Schrödinger equations) for chemically relevant areas. Second-order ODE will be covered in Week 4.

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.

$$\mathrm{I} + \mathrm{I} \rightarrow \mathrm{I}_2$$

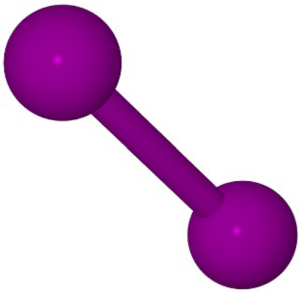


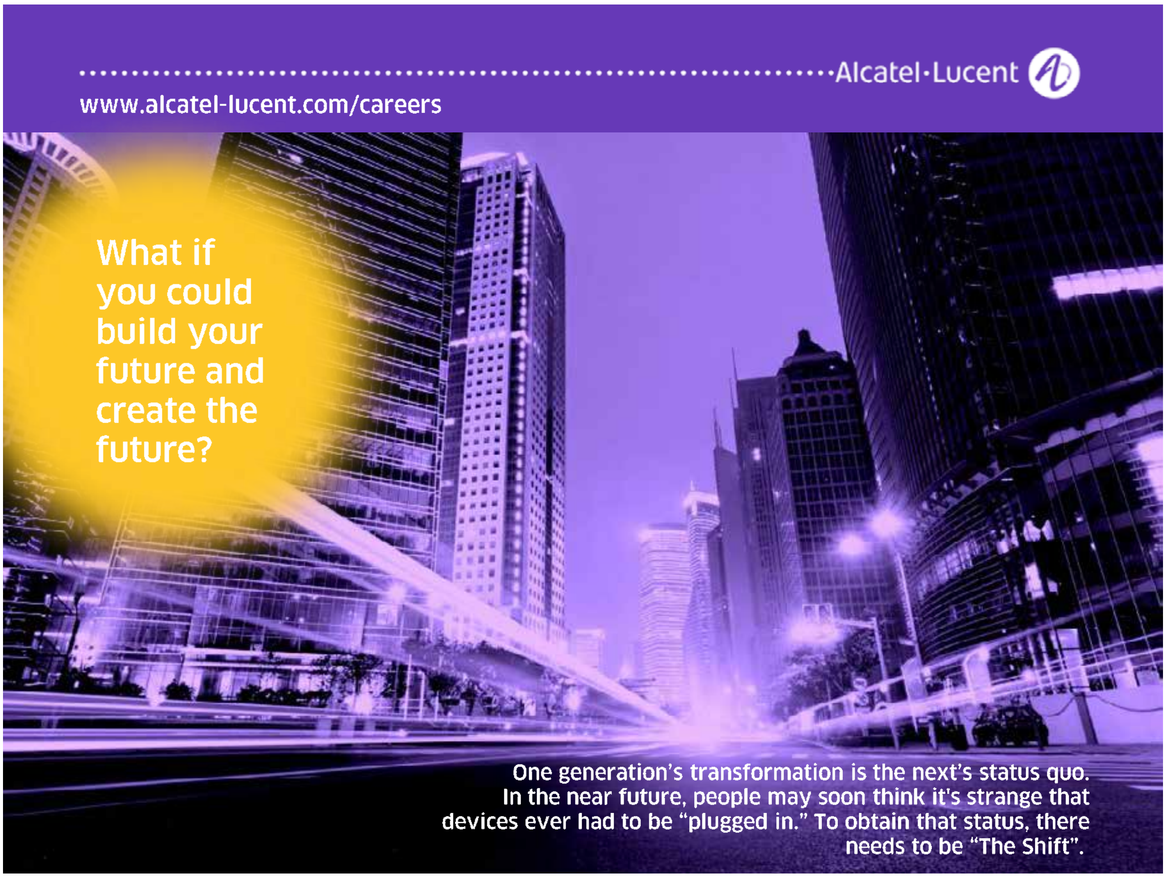
Figure 3.1: Iodine Molecule. I = purple.

The reaction is a second-order kinetics rate of loss of iodine atoms and follows the first-order ODE equation,

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

At 23°C in the gas phase this reaction has a rate constant $k = 7.0\times10^{9}$ L mol^{-1} s^{-1}. Using the separation of variables method solve this first-order ODE to find [I] 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 39)



3.2.2 Question 2: Beer-Lambert Law and the Absorption of Light by Molecules

In the lab 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. In the solution the intensity of light decreases as it moves away from the source owing to the absorption by molecules previously encountered. The probability of each absorption by a molecule is proportional to the "local" intensity of the light, and the number of molecules (that is concentrating times volume). Hence the decrease in intensity $-\mathrm{d}I$ of a parallel beam of light, per *unit area* of the solution, in a distance dx along the beam's direction due to a concentration of absorber molecules [A] is shown in Fig. 3.2.

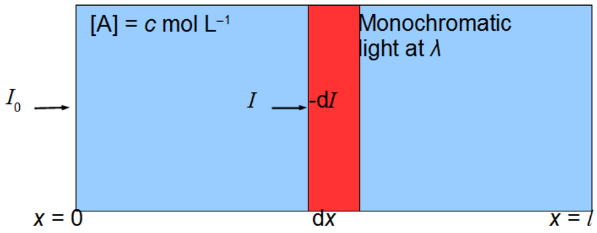


Figure 3.2: Quantitative Absorption of Light by a Molecule.

$$-\mathrm{d}I = (\text{constant})(\text{intensity of light})(\text{concentration of molecules})(\text{volume})$$

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

Where the constant, κ kappa, is the strength of absorption of the light of the given wavelength by the particular absorbing molecule, and the volume is a small length dx of *unit area.*

This gives the first-order ODE shown below.

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

1) Solve this first-order ODE for the intensity I if light transmitted through the total length of solution, l, assuming that the original intensity is I_0.
2) Convert your solution to a form consistent with $\log_{10}$ rather that natural logs. Convert kappa κ to the equivalent log to base 10 absorption coefficient, ε epsilon, with units of L mol^{-1} cm^{-1}.
3) Chlorophyll-a (Fig. 3.3) is one of the main photosynthetic pigments present in most plants that photosynthesize. It absorbs strongly in the 400-500 nm range and less strongly in the 650-700 nm range but lets most of the green-yellow light through and thus leaves appears greenish.

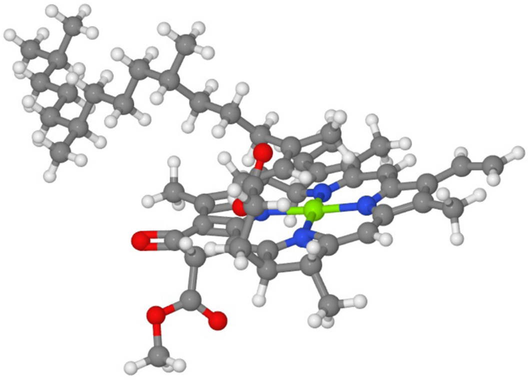


Figure 3.3: Chlorophyll-a. C = dark grey, H = grey, O = red, N = blue, Mg = green.

An analytical chemist needs to measure the concentration of chlorophyll-a. A solution (in methanol) 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 111,700 L mol^{-1} cm^{-1} at 417.8 nm, calculate the concentration of the chlorophyll

Jump to Solution 2 (see page 40)

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 ends and begins by a collision with another molecule which causes a random change in direction and the speed of movement. 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 high concentration towards low concentration.

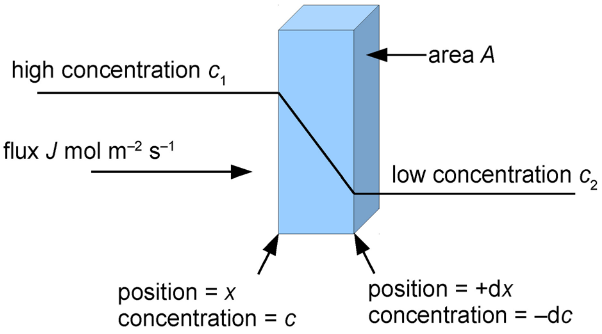


Figure 3.4: Linear Concentration Gradient of a Molecule.

For a linear concentration gradient as shown in Fig. 3.4 the flux of molecules diffusing is J mol m^{-2} s^{-1} and it is equal to

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}x}$$

The negative sign is for a positive flux from left to right, there is a negative concentration gradient from left to right. The diffusion constant D m^2 s^{-1} varies from one molecule to another and also depends upon the solvent molecule. The concentration gradient is $\mathrm{d}c/\mathrm{d}x$ mol L^{-1} m^{-1}. The above equation is the basis of Fick's First Law, but a more usable version of Fick's First Law is to note that the flux is the number of moles per area per second and write Fick's First Law as,

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -DA\frac{\mathrm{d}c}{\mathrm{d}x}$$

The average *net* distance, d, travelled (along the concentration gradient) by a molecule from its starting position during its random-walk in a time t is,

$$d = (2Dt)^{1/2}$$

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; and flames, combustion and explosions; to name but a few!

Sucrose has a diffusion constant in water at 20°C and 1 atmosphere pressure 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. Firstly, calculate how many moles of sucrose pass through the membrane in 10 minutes when the concentration difference is 0.1 mol L^{-1}. Secondly, calculate the average net distance, d, travelled by an individual sucrose molecule in this time.

Jump to Solution 3 (see page 42)

3.2.4 Question 4: The Average Speed of Gas Molecules

The distribution of speeds v (*i.e.* velocities ignoring the direction) of gas molecules is given by the Maxwell-Boltzmann speed distribution.

$$\frac{1}{N_0}\frac{\mathrm{d}N}{\mathrm{d}v} = f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\exp\left(-\frac{Mv^2}{2RT}\right)v^2$$

Where N is the number of molecules with speed v; N_0 is the total number of molecules; M is the molar mass; R is the gas constant; and T is the temperature. The average molecular speed v (pronounced "vee bar") is given by the integral of the above first-order ODE as

$$\bar{v} = \int_{v=0}^{v=\infty} v\, f(v)\,\mathrm{d}v \qquad \bar{v} = \int_{v=0}^{v=\infty} 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\exp\left(-\frac{Mv^2}{2RT}\right)v^2\, v\,\mathrm{d}v$$

Bringing the constants outside the integral gives

$$\bar{v} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_{v=0}^{v=\infty}\exp\left(-\frac{Mv^2}{2RT}\right)v^3\,\mathrm{d}v$$

Integrate this expression to find the average speed of gas molecules. Secondly, find the average speed of N_2 molecules (M = 28.02×10^{-3} kg mol^{-1}) at 298.15 K (25°C) given R = 8.3141 J K^{-1} mol^{-1}.

Jump to Solution 4 (see page 43)

3.3 Week 3 Tutorials Solutions

3.3.1 Solution 1: Recombination of Iodine Atoms in the Gas Phase

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

The separation of variables method is used to rearrange this first-order ODE so that the terms involving iodine atoms concentrations [I] are on the left and are separated from any constants and the other variable, time t, which are on the right hand side.

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

As the variables are now separated, the two sides of the equation may be separately integrated.

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

Any constants being placed outside the integral sign for clarity. Integrating the right hand side is straight forward. The foolproof way of handling the left hand side is to write the variable [I] as a numerator rather than a denominator.

$$\int [\mathrm{I}]^{-2}\,\mathrm{d}[\mathrm{I}] = -k\int \mathrm{d}t \qquad -[\mathrm{I}]^{-1} = -kt + C \qquad -\frac{1}{[\mathrm{I}]} = -kt + C$$

Where C is the constant of integration. Using the boundary condition that $[\mathrm{I}]_0 = 6.72\times10^{-3}$ mol L^{-1} at $t = 0$ s enables the constant of integration C to be eliminated. It is important that the symbols of these boundary conditions are used so that the nature of the variables is not lost.

$$\left[-\frac{1}{[\mathrm{I}]}\right]_{[\mathrm{I}]=[\mathrm{I}]_0}^{[\mathrm{I}]=[\mathrm{I}]} = -k[t]_{t=0}^{t=t} + C \qquad \left(-\frac{1}{[\mathrm{I}]}\right) - \left(-\frac{1}{[\mathrm{I}]_0}\right) = (-kt) - (k\times 0) + C - C$$

$$-\frac{1}{[\mathrm{I}]} + \frac{1}{[\mathrm{I}]_0} = -kt$$

Multiplying throughout by −1 gives,

$$\boxed{\frac{1}{[\mathrm{I}]} - \frac{1}{[\mathrm{I}]_0} = kt}$$

Now that the algebraic part of the integration of the first-order ODE is over, it is the time to substitute the physical quantities for the variable symbols.

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

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

$$\frac{1}{[\mathrm{I}]} = \left(1.05\times10^{10}\ \mathrm{L\,mol^{-1}}\right) + \left(1.4881\times10^{2}\ \mathrm{L\,mol^{-1}}\right) = 1.050\times10^{10}\ \mathrm{L\,mol^{-1}}$$

$$\boxed{[\mathrm{I}] = 9.5238\times10^{-11}\,\mathrm{mol\,L^{-1}}}$$

After 1.5 s the concentration of I atoms has dropped from 6.72×10^{-3} mol L^{-1} to 9.5238×10^{-11} mol L^{-1}.

Return to Question 1 (see page 34)

3.3.2 Solution 2: Beer-Lambert Law and the Absorption of Light by Molecules

1) The first-order ODE is,

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

Using the separation of variables method this may be integrated using the boundary condition of the original light intensity $I = I_0$ at $x = 0$ to the final limit $I = I$ and $x = l$.

$$\int_{I=I_0}^{I=I} \frac{\mathrm{d}I}{I} = -\kappa[\mathrm{A}]\int_{x=0}^{x=l} \mathrm{d}x \qquad [\ln I]_{I=I_0}^{I=I} = -\kappa[\mathrm{A}][x]_{x=0}^{x=l}$$

$$\ln(I) - \ln(I_0) = -\kappa[\mathrm{A}](l-0)$$

$$\boxed{\ln\left(\frac{I}{I_0}\right) = -\kappa[\mathrm{A}]l}$$

2) Converting this to logs to the base 10 gives,

$$\boxed{\log\left(\frac{I}{I_0}\right) = -\varepsilon[\mathrm{A}]l}$$

where we use $\ln x = (\ln 10)(\log x)$ and replace kappa by $\varepsilon = \kappa/\ln 10$ or $\varepsilon = \kappa/2.303$. The above log form of the absorption is called the Beer-Lamber Law and ε epsilon is the absorption coefficient (or more fully as the *decadic*

3)

$$\log\left(\frac{I}{I_0}\right) = -\varepsilon[\mathrm{A}]l \qquad \log\left(\frac{1.5}{100}\right) = -(111{,}700\ \mathrm{L\ mol^{-1}cm^{-1}})[\mathrm{A}](1.0\ \mathrm{cm})$$

$$[\mathrm{A}] = 1.6329\times 10^{-5}\ \mathrm{mol\ L^{-1}}$$

Notice how strongly the chlorophyll-a absorbs (98.5% light absorbed at this wavelength) for such a dilute solution.

Return to Question 2 (see page 36)

3.3.3 Solution 3: Diffusion of Molecules in Liquids, Gases or Solids

Fig. 3.5 shows the sucrose molecule.

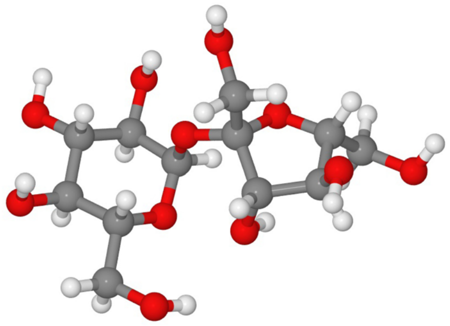


Figure 3.5: Sucrose Molecule. O = red, C = dark grey, H = grey.

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -DA\frac{\mathrm{d}c}{\mathrm{d}x} \qquad \frac{\mathrm{d}n}{\mathrm{d}t} = -(0.522\times 10^{-9}\ \mathrm{m^2s^{-1}})(2.4\times 10^{-6}\ \mathrm{m^2})\frac{-0.1\ \mathrm{mol\ L^{-1}}}{1.5\times 10^{-6}\ \mathrm{m}}$$

The units don't quite cancel, we need to convert L into m^3, also note that the concentration gradient is negative.

$$\mathrm{L} = \mathrm{dm^3} \qquad \mathrm{L} = (0.1\ \mathrm{m})^3 \qquad \mathrm{L} = 10^{-3}\ \mathrm{m^3}$$

$$0.1\ \mathrm{mol\ L^{-1}} = \left(0.1\ \frac{\mathrm{mol}}{\mathrm{L}}\right)\left(\frac{\mathrm{L}}{10^{-3}\ \mathrm{m^3}}\right) = 100\ \mathrm{mol\ m^{-3}}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -(0.522\times 10^{-9}\ \mathrm{m^2s^{-1}})(2.4\times 10^{-6}\ \mathrm{m^2})\frac{-100\ \mathrm{mol\ m^{-3}}}{1.5\times 10^{-6}\ \mathrm{m}}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 8.352\times 10^{-8}\ \mathrm{mol\ s^{-1}}$$

So in 10 minutes (or dt = 600 s) the change in the number of moles of sucrose is,

$$\mathrm{d}n = 5.0112\times 10^{-5}\ \mathrm{mol}$$

The average net distance travelled by a molecule of sucrose in 10 minutes is,

$$d = \sqrt{2Dt} = \sqrt{2\left(0.522\times 10^{-9}\ \mathrm{m^2 s^{-1}}\right)(600\ \mathrm{s})}$$

$$d = 7.9145\times 10^{-4}\ \mathrm{m}$$

Even though the sucrose is travelling at 100s of metres per second, the random-walk means that the diffusion distance it is less than 1 millimetre in 10 minutes at 20°C in a water solution. We must not confuse dn which has a roman d and which is the operator part of the differential, with the variable d (italic d) the random-walk distance.

Return to Question 3 (see page 37)

3.3.4 Solution 4: The Average Speed of Gas Molecules

$$\bar{v} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_{v=0}^{v=\infty}\exp\left(-\frac{Mv^2}{2RT}\right)v^3\,\mathrm{d}v$$

Most Chemistry textbooks gloss over this integration in order to save space as it is long 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 long-winded integration that you come across in your later career as a Chemist. Concentrating on the integral itself for the moment. For clarity let a be equal to the constants $a = M/2RT$ this gives the integral part of the equation as,

$$\int_{v=0}^{v=\infty}\exp\left(-av^2\right)v^3\,\mathrm{d}v$$

For our integral let us substitute $z = v^2$ then dz = 2v dv and the integral is then,

$$\int_{z=0}^{z=\infty}\exp(-az)\frac{z}{2}\,\mathrm{d}z$$

This is the integral of a product and is found by integrating by parts (Stroud & Booth 2007). Integration by parts makes use of the reverse of the product rule for differentiation. As a reminder, if u and v are functions of x then the differential of the product is

$$\frac{\mathrm{d}(uv)}{\mathrm{d}x} = u\frac{\mathrm{d}v}{\mathrm{d}x} + v\frac{\mathrm{d}u}{\mathrm{d}x}$$

Integrating both sides, then on the left hand side we arrive at the original function, a product of two terms.

$$uv = \int u\frac{\mathrm{d}v}{\mathrm{d}x}\mathrm{d}x + \int v\frac{\mathrm{d}u}{\mathrm{d}x}\mathrm{d}x$$

This is rearranged to to give the integration by parts.

$$\int u\frac{\mathrm{d}v}{\mathrm{d}x}\mathrm{d}x = uv - \int v\frac{\mathrm{d}u}{\mathrm{d}x}\mathrm{d}x$$

Cancelling out d*x* on the top and bottom gives us an aid to memory which may be remembered as,

$$\int u\,\mathrm{d}v = uv - \int v\,\mathrm{d}u$$

For clarity I have not included the constants of integration as they will eventually cancel out. After assigning the two functions *u* and d*v* we need to differentiate *u* and integrate d*v*. For our integral,

$$\int_{z=0}^{z=\infty} \exp(-az)\frac{z}{2}\,\mathrm{d}z$$

let us assign *u* and d*v* as,

$$u = \frac{z}{2} \qquad \mathrm{d}v = \exp(-az)\,\mathrm{d}z$$

Differentiating u and integrating dv gives,

$$\mathrm{d}u = \frac{\mathrm{d}z}{2} \qquad v = \frac{\exp(-az)}{-a}$$

Substituting in the terms u, du, v, and dv into the integration by parts equation gives,

$$\int_{z=0}^{z=\infty} \exp(-az)\frac{z}{2}\,\mathrm{d}z = uv - \int v\,\mathrm{d}u$$

$$\int_{z=0}^{z=\infty} \exp(-az)\frac{z}{2}\,\mathrm{d}z = \left[\frac{z}{2}\frac{\exp(-az)}{-a}\right]_{z=0}^{z=\infty} - \int_{z=0}^{z=\infty} \frac{\exp(-az)}{-a}\frac{\mathrm{d}z}{2}$$

$$\int_{z=0}^{z=\infty} \exp(-az)\frac{z}{2}\,\mathrm{d}z = \left[\frac{-z}{2a}\exp(-az) - \frac{1}{2a^2}\exp(-az)\right]_{z=0}^{z=\infty}$$

Applying the limits of infinity and zero for z gives,

$$\int_{z=0}^{z=\infty} \exp(-az)\frac{z}{2}\,\mathrm{d}z = (0-0) - \left(-0 - \frac{1}{2a^2}\right) = \frac{1}{2a^2}$$

We have now finished the integration and we have to substitute back, firstly for $a = M/2RT$,

$$\int_{z=0}^{z=\infty} \exp(-az)\frac{z}{2}\,\mathrm{d}z = \frac{1}{2a^2} = \frac{1}{2}\left(\frac{2RT}{M}\right)^2$$

$$\int_{v=0}^{v=\infty} \exp\left(-\frac{Mv^2}{2RT}\right)v^3\,\mathrm{d}v = \frac{1}{2}\left(\frac{2RT}{M}\right)^2$$

Our integral may now be substituted into the average speed of the molecule,

$$\bar{v} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_{v=0}^{v=\infty} \exp\left(-\frac{Mv^2}{2RT}\right)v^3\,\mathrm{d}v = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\frac{1}{2}\left(\frac{2RT}{M}\right)^2$$

In order to clean this up (and not get lost doing so) it is best to first write all the similar terms next to one another and write 4 as 2^2.

$$\bar{v} = \frac{2^2\,2^2}{2^{3/2}\,2}\,\frac{\pi}{\pi^{3/2}}\,\frac{M^{3/2}}{M^2}\,\frac{R^2}{R^{3/2}}\,\frac{T^2}{T^{3/2}}$$

Secondly bring all the terms from the denominator into the numerator, remembering that $x^a x^b = x^{a+b}$.

$$\bar{v} = 2^{(2+2-3/2-1)}\,\pi^{(1-3/2)}\,M^{(3/2-2)}\,R^{(2-3/2)}\,T^{(2-3/2)} = 2^{3/2}\,\pi^{-1/2}\,M^{-1/2}\,R^{1/2}\,T^{1/2}$$

$$\bar{v} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

This is a remarkably simple result of our integration by parts. The definition of the average speed is that there are the same number of molecules with less than the average speed as there are with more than the average speed. Fig. 3.6 shows the Maxwell-Boltzmann speed plot of the relative number of molecules against their speed. The axes are $y = f(v)/(4\pi(M/2\pi RT)^{3/2})$ and $x = v/(2RT/M)^{1/2}$ and the most probable speed $v_{mp} = (2RT/M)^{1/2}$ and average speed $v = (8RT/\pi M)^{1/2}$.

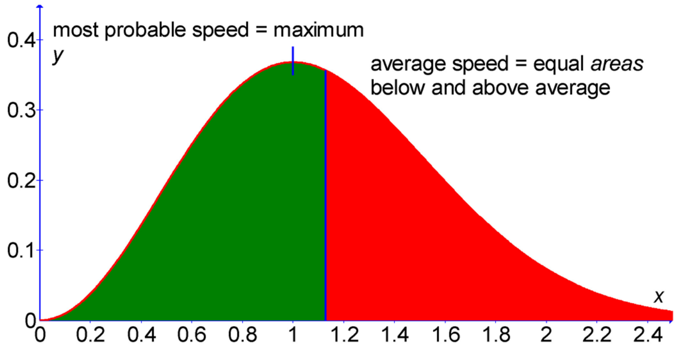


Figure 3.6: Maxwell-Boltzmann Speed Plot.

The average speed of N_2 at 298.15 K is,

$$\bar{v} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8(8.3141\ \mathrm{J\,K^{-1}mol^{-1}})(298.15\ \mathrm{K})}{\pi(28.02\times 10^{-3}\ \mathrm{kg\ mol^{-1}})}\right)^{1/2}$$

$$\bar{v} = 475\ \mathrm{m\ s^{-1}}$$

The units cancel when in the base SI units

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

The SI unit of mass is the kg not the gram. Although the average speed of the N_2 molecule is very large, because of diffusion (section 3.2.3), the average distance travelled by a N_2 molecule (the random walk distance) is only 5.5 *millimetre* per second (the diffusion constant for N_2 is $D = 1.5\times10^{-5}$ m^2 s^{-1}).

Return to Question 4 (see page 39)

4 Week 4: Chemistry and Second-Order Ordinary Differential Equations

We are now concentrating on second-order ODEs (see Section 3.1.2).

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 molecules moving in "infinitely" large space (that is infinitely large compared with the size of the molecule). The Schrödinger equation describes the wavefunctions for a particle of mass, m, moving in one-dimension, x, E is the total energy, the sum of the potential and the kinetic energy, it is constant and does vary with position and h is Planck's constant (see Section 3.1.2).

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

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 molecule as a function of its position in the one-dimension x. In our question we have free motion which means that the molecule is not subjected to any external forces. As the molecule experiences no forces the potential energy must be constant and we are free to define its value. If we let $V(x) = 0$ then the Schrödinger equations is simplified.

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

If our molecule is moving at velocity v then a general equation for its wavefunction is,

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

Solve the second-order ODE Schrödinger equation and find the total energy E of our molecule. 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 52)

4.1.2 Question 2: Movement of a Molecule in a One-Dimensional Box

Examples of this could be the motion of π-electrons in a conjugated polyene molecule or a molecule (such as an enzyme) confined in a carbon nano-tube. Fig. 4.1 shows a short single-walled nanotube (terminated with hydrogen atoms).

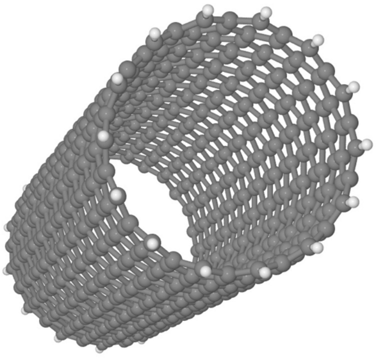


Figure 4.1: Nanotube Molecule. C = dark grey, H = grey.

For the Schrödinger equation

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

we have the particle confined to the box of length L, see Fig. 4.2.

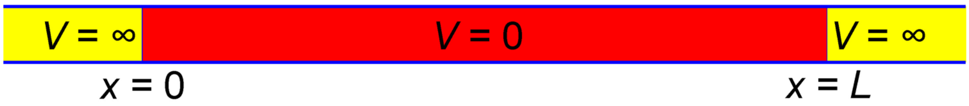


Figure 4.2: A One-Dimensional Box.

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.

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

The two infinite potential energy walls are the two boundary conditions for our second-order ODE. The wavefunction must be equal to zero, $\psi = 0$, at the two boundaries in order for the wave to "reflect" at the walls *exactly*, so the wavefunction can persist through time, that is the wavefunction is a *standing wave*. Quantum mechanics gives the trial wavefunction below.

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

Where $n = 1, 2, 3, 3, \ldots$ is the quantum number for the translational motion in one-dimension.

Firstly, solve the first-order ODE, the Schrödinger equation, by calculating the allowed energy levels using the trial wavefunction. Secondly, sketch the shapes of the first two allowed wavefunctions for $n = 1$ and for $n = 2$.

Jump to Solution 2 (see page 53)

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. This is an approximate model of the π-electrons in benzene where we treat the regular hexagon of benzene as a circle.

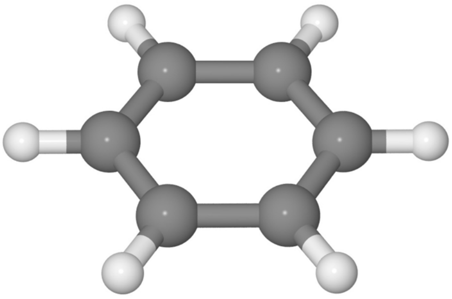


Figure 4.3: Benzene Molecule. C = dark grey, H = grey.

In the Schrödinger equation the potential energy for the π-electrons is constant around the ring, and thus may be set equal to zero, $V(x) = 0$, where x is the distance around the circumference.

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

For the general equation of a wave we have,

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

Where λ is the wavelength of our wavefunction. In order to be a standing wave and persist through time the wavefunction must satisfy a cyclic boundary condition that the wavelengths must fit exactly into the circumference, *i.e.* there are an integral number of wavelengths in the circumference, see Fig. 4.4.

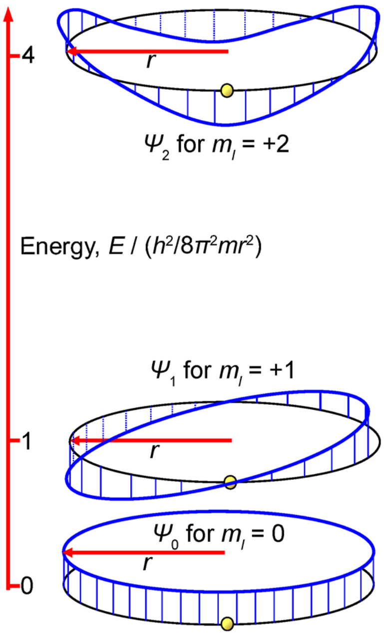


Figure 4.4: Wavefunctions (Blue) for a Particle on a Ring (Black).

The shapes of the wavefunctions are shown in Fig. 4.4, the wavefunction has a uniform amplitude around the ring for ψ_0, with one wavelength for ψ_1 and with two wavelengths for ψ_2. Using Maths this cyclic boundary condition of an integral number of wavelengths fitting the circumference of the ring is equivalent to,

$$m_l\lambda = 2\pi r \quad \text{where} \quad m_l = 0, \pm 1, \pm 2, \pm 3, \cdots$$

The quantum number for rotational motion has, by convention, the symbol m_l (don't confuse this m for the mass of the particle). The plus and minus values are for the particle to move clockwise or anti-clockwise around the ring. But changing the direction of rotation (positive or negative values of m_l) does not change the energy of the wavefunction. For $m_l = 0$ the particle has the same probability of being found anywhere on the ring. The trial wavefunction for the particle on a ring is given below.

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

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

Jump to Solution 3 (see page 56)

4.1.4 Question 4: Motion of a Particle on a Ring, 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 $m_1 = 0$, 2 π-electrons in $m_1 = -1$ and 2 π-electrons in $m_1 = +1$, and so the highest occupied molecular orbitals (HOMO) are $m_1 = \pm 1$ and the lowest unoccupied molecular orbitals (LUMO) are $m_1 = \pm 2$ (see Fig. 4.5).

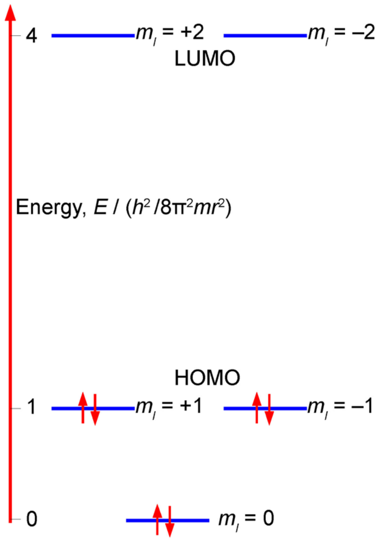


Figure 4.5: Benzene π-Electron Energies for the Particle on a Ring Model.

The C-C bond distance in benzene is 1.40 Å and so for the regular hexagon the radius $r = 1.40$ Å may be used in the approximation of treating it as a circular ring.

Calculate the wavelength of light that would be absorbed in order to excite the transition from $m_1 = \pm 1$ to $m_1 = \pm 2$, using the allowed energy equation that you derived for Question 3, the energy of a photon of light and the equation for the wave-nature of light.

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

The values of the physical quantities are $h = 6.6261\times10^{-34}$ J s; $m = 9.1094\times10^{-31}$ kg; $r = 1.40\times10^{-10}$ m; $c = 2.9979\times10^{8}$ m s^{-1}.

Jump to Solution 4 (see page 52)

4.2 Week 4 Tutorial Solutions

4.2.1 Solution 1: Unconstrained Movement of a Molecule in One-Dimension

The simplified Schrödinger equation is in a constant potential energy, and we may define it as zero potential energy,

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

Firstly the second derivative of ψ must be calculated from the general wavefunction,

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

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

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

Taking out the common factor outside brackets gives,

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

The term on the right hand side involving sin and cos and it is the same as the wavefunction ψ, thus the second derivative is quite simple,

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi m v}{h}\right)^2 \psi$$

Substituting the second derivative into the Schrödinger equation with $V(\psi) = 0$,

$$\frac{h^2}{8\pi^2 m}\left(\frac{2\pi m v}{h}\right)^2 \psi = E\psi$$

The wavefunction ψ cancels both sides and the total energy is,

$$E = \frac{h^2}{8\pi^2 m}\left(\frac{2\pi m v}{h}\right)^2$$

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

The *unconstrained* motion of the molecule has the same energy as the classical Newtonian translational energy and is *non-quantized*. It is the presence of the boundary conditions which leads to the quantization and if the one-dimensional box is infinite it does not have any boundary conditions.

Return to Question 1 (see page 47)

4.2.2 Solution 2: Movement of a Molecule in a One-Dimensional Box

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

The trial wavefunction is differentiated twice.

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

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2}{L}\right)^{1/2}\left(\frac{n\pi}{L}\right)^2 \sin\left(\frac{n\pi x}{L}\right)$$

Part of the right hand side is recognisable as our trial wavefunction, substitution of which gives the second derivative below.

$$\frac{d^2\psi}{dx^2} = -\left(\frac{n\pi}{L}\right)^2 \psi$$

We can now substitute our second derivative back into the Schrödinger equation with zero potential energy.

$$\frac{-h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E\psi \qquad -\frac{h^2}{8\pi^2 m}\left(-\left(\frac{n\pi}{L}\right)^2\psi\right) = E\psi \qquad \frac{n^2h^2\pi^2}{8\pi^2 mL^2}\psi = E\psi$$

Cancelling out where possible.

$$\boxed{E = \frac{n^2h^2}{8mL^2} \quad \text{where} \quad n = 1,2,3,\ldots}$$

These are the allowed energy levels (the units cancel out to be J, remembering that J = kg m^2 s^{-1}). This "bounded" motion has quantized solutions whereas the "unbounded" motion of Question 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. The lowest two allowed wavefunctions may be sketched for the wavefunction with $n = 1$ and $n = 2$,

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

Using your calculator, set the mode to radians rather than degrees, and note down the values for sin(0), sin(π/8), sin(π/4), sin(3π/8), sin(π/2), sin(5π/8), sin(3π/4), sin(7π/8), sin(π) you can use these values to sketch the wavefunctions for $n = 1$. Using a similar method will enable you to sketch the wavefunction for $n = 2$, as in Fig 4.6 with the wavefunctions in red.

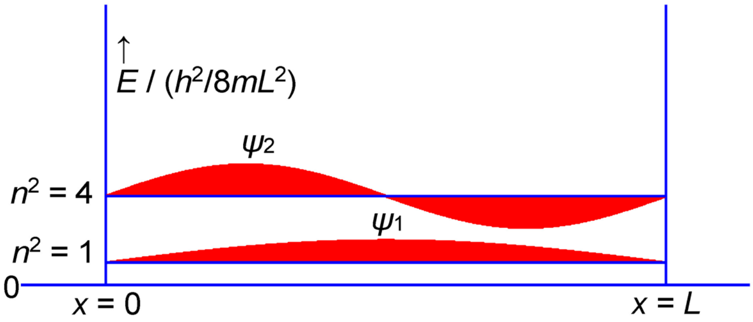


Figure 4.6: Wavefunctions for $n = 1$ and $n = 2$ for a Particle in a One-Dimensional Box.

In Fig. 4.6 the wavefunction (in red) has one maximum for $n = 1$, and the wavefunction has two maxima for $n = 2$. On the other hand, the total allowed energies (in blue) E_1 and E_2 are both constant and don't vary with the position of the particle in the box.

Return to Question 2 (see page 48)

4.2.3 Solution 3: Motion of a Particle on a Ring

Calculating the second derivative for the wavefunction.

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

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

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

Recognising the original wavefunction in the right hand side of the second derivative, gives,

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\left(\frac{m_l}{r}\right)^2\psi$$

The second derivative is substituted in the Schrödinger equation and then terms cancelled where possible.

$$-\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \qquad -\frac{h^2}{8\pi^2 m}\left(-\frac{m_l^2}{r^2}\right)\psi = E\psi$$

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

Return to Question 3 (see page 49)

4.2.4 Solution 4: Motion of a Particle on a Ring, Absorption Spectrum of Benzene

$$E = \frac{m_l^2 h^2}{8\pi^2 m r^2} \qquad E_1 = \frac{h^2}{8\pi^2 m r^2} \qquad E_2 = \frac{4h^2}{8\pi^2 m r^2}$$

The energy of the transition in benzene due to the absorption of a photon is $\Delta E = (E_2 - E_1)$ and substituting the values for the physical quantities $h = 6.6261\times10^{-34}$ J s; $m = 9.1094\times10^{-31}$ kg; $r = 1.40\times10^{-10}$ m; $c = 2.9979\times10^{8}$ m s^{-1} we have,

$$\Delta E = \frac{3h^2}{8\pi^2 m r^2} \qquad \Delta E = \frac{3\left(6.6261\times 10^{-34}\ \mathrm{J\ s}\right)^2}{8\pi^2\left(9.1094\times 10^{-31}\ \mathrm{kg}\right)\left(1.40\times 10^{-10}\ \mathrm{m}\right)^2}$$

Remembering that J = kg m^2 s^{-2} this gives,

$$\Delta E = 9.3433\times 10^{-19}\ \mathrm{J}$$

Notice how molecular energies of single molecules are of the order 10^{-19} J. The wavelength required to be absorbed is calculated by the following method.

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

$$\lambda = \frac{ch}{E_{\text{photon}}} = \frac{\left(2.9979\times 10^{8}\ \mathrm{m\ s^{-1}}\right)\left(6.6261\times 10^{-34}\ \mathrm{J\ s}\right)}{9.3433\times 10^{-19}\ \mathrm{J}}$$

$$\lambda = 2.126\times 10^{-7}\ \mathrm{m} = 213\ \mathrm{nm}$$

Using the normal units for UV-visible light the wavelength is predicted to be 213 nm by the approximate treatment. Fig. 4.7 shows that experimentally the absorption is at $\lambda_{\text{max}} \approx 255$ nm, so the agreement is pretty good for this *first* approximation.

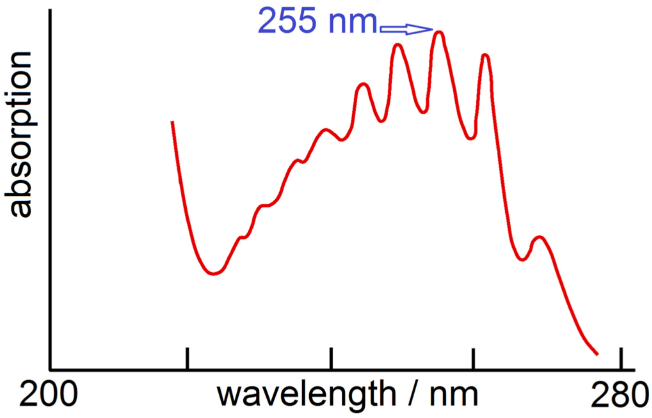


Figure 4.7: Absorption Spectrum of Benzene Vapour.

Return to Question 4 (see page 51)

5 Week 5: Chemistry and Advanced Integration

This weeks 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 a solid 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. Dissolution is used in analytical chemistry, metal extraction from their ores, nuclear waste reprocessing, in the pharmaceutical industry, chemical engineering and biological processes. Fig. 5.1 shows dissolution in a simple diagrammatic fashion.

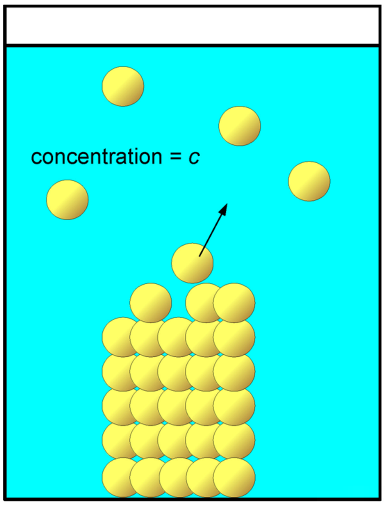


Figure 5.1: Dissolution of a Solid Crystal in a Solvent.

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), then the concentration of the solid in solution, *c*, after a time *t* will be determined by the following integral.

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

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

Jump to Solution 1 (see page 62)

5.1.2 Question 2: Population of Diatomic Molecules in Rotational Quantum Levels

Molecules are always on the move and also they rotate and vibrate. Quantum mechanics dictates that the rotations and vibrations can only occur at certain frequencies. Fig. 5.2 shows the rotation of an HCl molecule around its centre of gravity (or centre of mass).

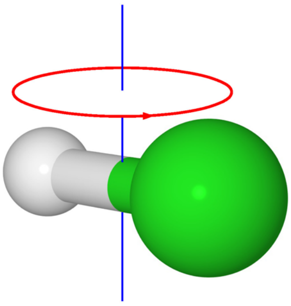


Figure 5.2: Rotation of an HCl Molecule around its Centre of Gravity.
H = grey and Cl = green.

If you want to calculate the population of diatomic molecules, such as HCl, in the various rotational energy levels, you need to solve the following integral that defines something called the rotational partition function q_r.

$$q_r = \int_{J=0}^{J=\infty} (2J+1) \exp\left(-\frac{J(J+1)h^2}{8\pi^2 I k_B T}\right) dJ$$

I is a constant for a give molecule (called the moment of inertia); h is Planck's constant; k_B is Boltzmann's constant and T is the absolute temperature (constant at a fixed temperature). The rotational quantum number J can have only 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 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 substitution $z = J(J + 1)$.

Jump to Solution 2 (see page 63)

5.1.3 Question 3: Chemistry and Normalization of Wavefunctions

The 1*s* orbital is the lowest electronic state of a hydrogen atom. The following radial probability distribution function,

$$P = N r^2 \exp\left(-\frac{2r}{a_0}\right)$$

describes the probability, P, of finding the electron at a distance, r, from the nucleus, with a_0 being a constant (the Bohr radius or the most likely distance) and P is related to the square of the wavefunction. N is an unknown constant, the normalization constant, which ensures that the Maths equation above makes chemical common sense that the probability of finding the electron anywhere within the hydrogen atom must be 1. In mathematical notation this translates to the equation below.

$$\int_{r=0}^{r=\infty} P \, \mathrm{d}r = 1$$

The probability density function that satisfy this condition are said to be *normalized*. Determine the normalization constant and thus the normalized radial probability function P (we will need to use integration by parts twice to evaluate the integral).

Jump to Solution 3 (see page 64)

5.1.4 Question 4: Computational Chemistry

Integrals of the type

$$I_1 = \int_{r=0}^{r=\infty} r \exp(-a r^2) \, \mathrm{d}r \quad \text{and} \quad I_2 = \int_{r=0}^{r=\infty} r^2 \exp(-a r^2) \, \mathrm{d}r$$

are important in computational chemistry where computer packages are used to find solutions to the Schrödinger equation of molecular wavefunctions. Such computer programs model molecular structures, chemical reaction profiles and thermodynamic properties and are widely used in chemical and biological research both in industry and in universities, *e.g.* the structure and interactions of drug molecules. Since the exact molecular orbitals are highly complex, they are approximated by "Gaussian wavefunctions" that all contain the exponential $\exp(-ar^2)$ multiplied by a polynomial r^n which are much easier to integrate. The use of Gaussian functions leads to integrals such as those shown above.

Calculate the above integrals using (a) the substitution method for I_1 and (b) integration by parts for I_2, and making use of the integral below,

$$I_0 = \int_{r=0}^{r=\infty} \exp(-a r^2)\, \mathrm{d}r = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

Jump to Solution 4 (see page 67)

5.1.5 Question 5: Spectroscopy and Fourier Transform

Certain spectroscopic characterization methods such as nuclear magnetic resonance, infrared and Raman spectroscopies and some types of mass spectrometry give a spectrum of several peaks of various intensities at particular frequencies. This "normal" spectrum is called a frequency domain spectrum and consists of intensity, F, as a function of frequency, ω. The frequency domain spectrum is described by the mathematical equation $F(\omega)$ which can be recorded experimentally by scanning a wide range of frequencies. However, such a conventional scan may take some considerable time.

In many cases (magnetic resonance or infrared spectroscopy) it is more practical and takes a considerably shorter time to simply excite molecules with a pulse of a broad range of frequencies all at once and then measure the change of the total signal intensity with time t instead. This is called the time domain or free induction decay (FID) signal. This time domain signal usually happens within a few seconds and thus the data collection has been speeded up orders of magnitude compared with the classic frequency domain technique. Let us take the simplest case possible where the signal decays exponentially with time the measurement yields a time domain signal intensity $f(t)$ proportional to e^{-at} where a is a decay constant.

The frequency domain spectrum $F(\omega)$, which is what the chemist needs to be able to understand the Chemistry of the molecule, is obtained from the time domain signal $f(t)$ by a mathematical technique called a Fourier transform and requires the solution of the integral below.

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

Note that the product of time t (units s) and frequency ω (units s^{-1}) gives a dimensionless variable. For $f(t) = \exp(-at)$ find (using integration by parts twice) the solution of the integral shown below.

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

Jump to Solution 5 (see page 69)

5.1.6 Question 6: Integrated Rate Law for a 2nd order Reaction with Two Reactants

For a reaction where two different compounds A and B react with each other,

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

the rate of reaction, v, *may* depend on the concentrations of both A and B molecules (in which case the reaction is called a second-order reaction). An example is one of the atmospheric reactions that occur in the stratosphere for air that is polluted with chlorine containing molecules (both natural and man-made),

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

The molecule nitrosyl chloride is shown in Fig. 5.3.

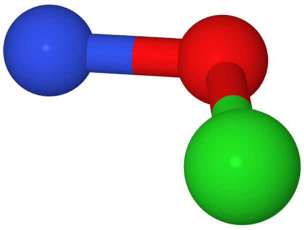


Figure 5.3: Nitrosyl Chloride Molecule. N = blue, O = red, Cl = green.

The rate of reaction, v, for a second-order reaction with two different reactants is,

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

The starting concentrations of reactants at time $t = 0$ being $[\mathrm{A}]_0$ mol L^{-1} for A and $[\mathrm{B}]_0$ mol L^{-1} for B and with no products C or D initially present. After a certain time t there will be x moles of C and D, our two products, while x moles of A and B will have been consumed. The kinetics of such a reaction describe the changes of concentration with time. In mathematical terms this leads to the following integrated rate law.

$$\int_0^x \frac{1}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)}\,\mathrm{d}x = kt$$

Where k is the rate constant and describes how fast the reaction occurs. Calculate the integral using partial fractions (see Parker 2011, section 1.3.8) and describe the graph you would plot to confirm this integrated equation is chemically correct.

Jump to Solution 6 (see page 72)

5.2 Week 5 Tutorial Solutions

5.2.1 Solution 1: Dissolution of a Solid by a Solvent

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

To integrate the above equation describing a solid dissolving in a solvent we (1) substitute for the denominator; (2) differentiate the substitution; and (3) rearrange to obtain a substitute for dc.

$$z = c_s - c \qquad \frac{\mathrm{d}z}{\mathrm{d}c} = -1 \qquad \mathrm{d}c = -\mathrm{d}z$$

Note that the integral limits also must change when we make the substitution $z = c_s - c$. The lower limit $c = 0$ becomes $z = c_s$. The upper limit at $c = c$ becomes $z = c_s - c$. These may now be substituted into the integral.

$$\int_{c=0}^{c=c} \frac{1}{c_{\mathrm{s}} - c}\, \mathrm{d}c = k\,t \qquad -\int_{z=c_{\mathrm{s}}}^{z=c_{\mathrm{s}}-c} \frac{1}{z}\, \mathrm{d}z = k\,t \qquad \Big[-\ln(z)\Big]_{z=c_{\mathrm{s}}}^{z=c_{\mathrm{s}}-c} = k\,t$$

$$-\ln(c_{\mathrm{s}} - c) + \ln(c_{\mathrm{s}}) = k\,t \qquad \ln\left(\frac{c_{\mathrm{s}} - c}{c_{\mathrm{s}}}\right) = -k\,t$$

$$\frac{c_{\mathrm{s}} - c}{c_{\mathrm{s}}} = \exp(-k\,t) \qquad c_{\mathrm{s}} - c = c_{\mathrm{s}} \exp(-k\,t)$$

$$c = c_{\mathrm{s}}\big(1 - \exp(-k\,t)\big)$$

Thus the dissolution of the solid molecule by the solvent is initially relatively fast and then slows up exponentially as the solution concentration approaches that of the saturated solution.

Return to Question 1 (see page 57)

5.2.2 Solution 2: Population of Diatomic Molecules in Rotational Quantum Levels

$$q_{\mathrm{r}} = \int_{J=0}^{J=\infty} (2J+1)\exp\left(-\frac{J(J+1)h^2}{8\pi^2 I k_{\mathrm{B}} T}\right) \mathrm{d}J$$

The substitution is differentiated with respect d*J* as follows.

$$z = J(J+1) = J^2 + J \qquad \frac{\mathrm{d}z}{\mathrm{d}J} = 2J+1 \qquad \mathrm{d}J = \frac{1}{2J+1}\,\mathrm{d}z$$

You must also check what happens to the integration limits. The lower limit, $J = 0$, becomes $z = 0$, and the upper limit $J = \infty$ will become $z = \infty$. The substitution in the integral gives the following integral, but note that he $(2J + 1)$ terms cancel out top and bottom,

$$q_{\mathrm{r}} = \int_{z=0}^{z=\infty} (2J+1)\exp\left(-\frac{z\,h^2}{8\pi^2 I k_{\mathrm{B}} T}\right) \frac{1}{2J+1}\,\mathrm{d}z$$

$$q_{\mathrm{r}} = \int_{z=0}^{z=\infty} \exp\left(-\frac{z\,h^2}{8\pi^2 I k_{\mathrm{B}} T}\right) \mathrm{d}z$$

All the constants that are independent of *z* are grouped together as *A* and the integral then simplifies to,

$$A = \frac{h^2}{8\pi^2 I k_{\mathrm{B}} T} \qquad q_{\mathrm{r}} = \int_{z=0}^{z=\infty} \exp(-A\,z)\,\mathrm{d}z$$

Its integration gives the exponential function divided by the constant −*A*. The integration constant *C* is left out since it will cancel-out at the subtraction stage of the definite integral. From the shape of the negative exponential (Fig. 1.2) when $z = 0$ then $\exp(-Az) = 1$ and when $z = \infty$ then $\exp(-Az) = 0$.

$$q_r = \left[\frac{\exp(-Az)}{-A}\right]_{z=0}^{z=\infty} \qquad q_r = \frac{0}{-A} - \frac{1}{-A} = \frac{1}{A}$$

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

The rotational partition function is just the reciprocal of *A*, the collection of constants for the given molecule at a given temperature. Your Chemistry in later years will use this value for q_r to calculate the population of molecules occupying a given rotational quantum level *J* at a chosen temperature and also total the rotational energy of a mole of molecules at this temperature.

Return to Question 2 (see page 58)

5.2.3 Solution 3: Chemistry and Normalization of Wavefunctions

To find whether the probability distribution function, *P*, is normalized we have to integrate the following and show it is equal to unity.

$$\int_{r=0}^{r=\infty} N\, r^2 \exp\left(-\frac{2r}{a_0}\right) \mathrm{d}r = 1$$

As *N* is a constant let's move it outside the integral.

$$N \int_{r=0}^{r=\infty} r^2 \exp\left(-\frac{2r}{a_0}\right) \mathrm{d}r = 1$$

We make use of integration by parts (see section 3.3.4).

$$\int u\, \mathrm{d}v = uv - \int v\, \mathrm{d}u$$

Let us set the easier part of the equation to differentiate to be equal to *u*.

$$u = r^2 \qquad \frac{\mathrm{d}u}{\mathrm{d}r} = 2r \qquad \mathrm{d}u = 2r\, \mathrm{d}r$$

$$\mathrm{d}v = \exp\left(-\frac{2r}{a_0}\right) \mathrm{d}r \qquad v = \int \exp\left(-\frac{2r}{a_0}\right) \mathrm{d}r \qquad v = -\frac{a_0}{2} \exp\left(-\frac{2r}{a_0}\right)$$

Using integration by parts gives,

$$\int_{r=0}^{r=\infty} P\, \mathrm{d}r = N\left(\left[r^2 \frac{-a_0}{2} \exp\left(-\frac{2r}{a_0}\right)\right]_{r=0}^{r=\infty} - \int_{r=0}^{r=\infty} \frac{-a_0}{2} \exp\left(-\frac{2r}{a_0}\right) 2r\, \mathrm{d}r\right) = 1$$

Cleaning this up a little gives,

$$\int_{r=0}^{r=\infty} P\, \mathrm{d}r = N\left(\left[\frac{-a_0 r^2}{2} \exp\left(-\frac{2r}{a_0}\right)\right]_{r=0}^{r=\infty} + \int_{r=0}^{r=\infty} a_0 r \exp\left(-\frac{2r}{a_0}\right) \mathrm{d}r\right) = 1$$

This is the intermediate result from applying integration by parts once. The second term in the brackets is evaluated by using integration by parts a second time.

$$\int_{r=0}^{r=\infty} a_0 r \exp\left(-\frac{2r}{a_0}\right) \mathrm{d}r$$

$$u = r \qquad \frac{\mathrm{d}u}{\mathrm{d}r} = 1 \qquad \mathrm{d}u = \mathrm{d}r$$

$$\mathrm{d}v = \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r \qquad v = \int \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r \qquad v = -\frac{a_0}{2}\exp\left(-\frac{2r}{a_0}\right)$$

$$\int_{r=0}^{r=\infty} a_0 r \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r = a_0\left(\left[r\frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)\right]_{r=0}^{r=\infty} - \int_{r=0}^{r=\infty}\frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r\right)$$

Tidying up the first term and integrating the second one gives,

$$\int_{r=0}^{r=\infty} a_0 r \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r = a_0\left(\left[\frac{-a_0 r}{2}\exp\left(-\frac{2r}{a_0}\right)\right]_{r=0}^{r=\infty} + \frac{a_0}{2}\left[\frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)\right]_{r=0}^{r=\infty}\right)$$

When this has the brackets removed it cleans up to,

$$\int_{r=0}^{r=\infty} a_0 r \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r = \left[\frac{-a_0^2 r}{2}\exp\left(-\frac{2r}{a_0}\right) - \frac{a_0^3}{4}\exp\left(-\frac{2r}{a_0}\right)\right]_{r=0}^{r=\infty}$$

Substituting the above equation for the second term in the brackets of our intermediate (yellow high lighted) result gives,

$$\int_{r=0}^{r=\infty} P\,\mathrm{d}r = N\left[-\frac{a_0 r^2}{2}\exp\left(-\frac{2r}{a_0}\right) - \frac{a_0^2 r}{2}\exp\left(-\frac{2r}{a_0}\right) - \frac{a_0^3}{4}\exp\left(-\frac{2r}{a_0}\right)\right]_{r=0}^{r=\infty} = 1$$

At the upper limit of $r = \infty$ the exponential functions will go *faster* towards zero than either r^2 or r goes to infinity, so that all 3 terms become zero for the upper limit. At the lower limit of $r = 0$ the exponential functions will all be 1 whereas the first two terms with the pre-exponential factor involving r^2 or r will become zero,

$$\int_{r=0}^{r=\infty} P\,\mathrm{d}r = N\left(0 - 0 - 0 + 0 + 0 + \frac{a_0^3}{4}\right) = 1$$

$$N = \frac{4}{a_0^3}$$

We have now found the normalization constant and this allows us to write the normalized probability density function for the hydrogen atom 1*s* electron.

$$P = \frac{4}{a_0^3}r^2\exp\left(-\frac{2r}{a_0}\right)$$

Fig. 5.4 is a graph of P against r using a_0 = 0.5292 Å for the Bohr radius. The total integrated area under the probability distribution function is unity, *i.e.* there is 100% probability that the 1*s* electron of the H-atom is between $r = 0$ and $r = \infty$.

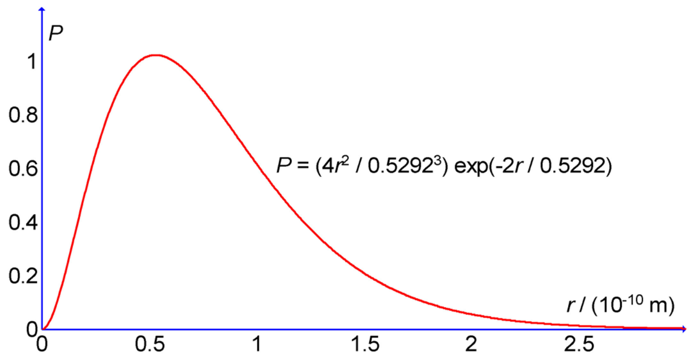


Figure 5.4: Hydrogen Atom 1*s* Radial Distribution Function.

Return to Question 3 (see page 59)

5.2.4 Solution 4: Computational Chemistry

For solving the integral I_1 we integrate by using the substitution as show below,

$$I_1 = \int_{r=0}^{r=\infty} r \exp(-ar^2)\,\mathrm{d}r$$

$$z = ar^2 \qquad \frac{\mathrm{d}z}{\mathrm{d}r} = 2ar \qquad \mathrm{d}r = \frac{1}{2ar}\,\mathrm{d}z$$

When substituted into I_1 and noting that the integration limits don't change for this substitution, we obtain,

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

$$I_1 = \frac{1}{2a} \left[-\exp(-z)\right]_{z=0}^{z=\infty} \qquad I_1 = \frac{1}{2a}[-0+1]$$

$$\boxed{I_1 = \frac{1}{2a}}$$

The integral I_2 may be written as below where I have explicitly written r^2 as $r \times r$ in the pre-exponential term and then integrated by parts,

$$I_2 = \int_{r=0}^{r=\infty} r^2 \exp(-ar^2) \mathrm{d}r = \int_{r=0}^{r=\infty} r \left(r \exp(-ar^2)\right) \mathrm{d}r$$

$$\int u \, \mathrm{d}v = uv - \int v \, \mathrm{d}u$$

Let us choose for u and $\mathrm{d}v$ as

$$u = r \qquad \mathrm{d}u = \mathrm{d}r$$

$$\mathrm{d}v = r \exp(-ar^2) \mathrm{d}r \qquad v = \int r \exp(-ar^2) \mathrm{d}r$$

The easiest way of obtaining the integral for v is to substitute

$$t = r^2 \qquad \mathrm{d}t = 2r \mathrm{d}r \qquad \frac{1}{2}\mathrm{d}t = r \mathrm{d}r$$

$$v = \int \frac{1}{2} \exp(-at) \mathrm{d}t \qquad v = -\frac{1}{2a} \exp(-at)$$

Substituting back in for t gives,

$$v = -\frac{1}{2a} \exp(-ar^2)$$

We can now use the integration by parts for I_2 where I have explicitly written r^2 as $r \times r$ in the pre-exponential term,

$$I_2 = \int_{r=0}^{r=\infty} r \left(r \exp(-ar^2)\right) \mathrm{d}r$$

Using the following for u, du, dv, and v,

$$u = r \qquad \mathrm{d}u = \mathrm{d}r$$

$$\mathrm{d}v = r\exp\left(-ar^2\right)\mathrm{d}r \qquad v = -\frac{1}{2a}\exp\left(-ar^2\right)$$

$$I_2 = \left[r\,\frac{-1}{2a}\exp\left(-ar^2\right)\right]_{r=0}^{r=\infty} + \frac{1}{2a}\int_{r=0}^{r=\infty}\exp\left(-ar^2\right)\mathrm{d}r$$

At the upper limit of infinity the exponential function will go faster towards zero than r goes to infinity. At the lower limit the exponential term will give 1 but r will be zero.

$$I_2 = [-0+0] + \frac{1}{2a}\int_{r=0}^{r=\infty}\exp\left(-ar^2\right)\mathrm{d}r = \frac{1}{2a}\int_{r=0}^{r=\infty}\exp\left(-ar^2\right)\mathrm{d}r$$

Question 4 gives us the standard integral for I_0,

$$I_0 = \int_{r=0}^{r=\infty}\exp\left(-ar^2\right)\mathrm{d}r = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$I_2 = \frac{1}{2a}\int_{r=0}^{r=\infty}\exp\left(-ar^2\right)\mathrm{d}r = \frac{1}{2a}\,\frac{1}{2}\sqrt{\frac{\pi}{a}}$$

So the two Gaussian integrals used in quantum Chemistry to solve complex molecular structures and reaction pathways are,

$$I_1 = \frac{1}{2a} \quad \text{and} \quad I_2 = \frac{1}{4a}\sqrt{\frac{\pi}{a}}$$

Return to Question 4 (see page 59)

5.2.5 Solution 5: Spectroscopy and Fourier Transform

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

We need to integrate by parts $\int u\,\mathrm{d}v = uv - \int v\,\mathrm{d}u$, and after we assign the two functions u and dv we will need to differentiate u and integrate dv.

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

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \exp(-at) \qquad v = \int \exp(-at)\,\mathrm{d}t \qquad v = -\frac{\exp(-at)}{a}$$

Applying integration by parts gives but keeping the √(2/π) aside for the moment for clarity, we have,

$$\int_{t=0}^{t=\infty} \cos(\omega t)\exp(-at)\,\mathrm{d}t = \left[-\cos(\omega t)\frac{\exp(-at)}{a}\right]_{t=0}^{t=\infty} - \int_{t=0}^{t=\infty} \frac{-\exp(-at)}{a}(-\omega\sin(\omega t))\,\mathrm{d}t$$

$$\int_{t=0}^{t=\infty} \cos(\omega t)\exp(-at)\,\mathrm{d}t = \left[0-\left(-1\frac{1}{a}\right)\right] - \frac{\omega}{a}\int_{t=0}^{t=\infty} \exp(-at)\sin(\omega t)\,\mathrm{d}t$$

$$\int_{t=0}^{t=\infty} \cos(\omega t)\exp(-at)\,\mathrm{d}t = \frac{1}{a} - \frac{\omega}{a}\int_{t=0}^{t=\infty} \exp(-at)\sin(\omega t)\,\mathrm{d}t$$

This intermediate result leaves us with the problem of finding a solution to another integral which once again is carried out using integration by parts, this time with,

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

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \exp(-at) \qquad v = \int \exp(-at)\,\mathrm{d}t \qquad v = -\frac{\exp(-at)}{a}$$

The sine integral (the second term on the right hand side) in the intermediate result becomes,

$$\int_{t=0}^{t=\infty} \exp(-at)\sin(\omega t)\,\mathrm{d}t = \left[-\sin(\omega t)\,\frac{\exp(-at)}{a}\right]_{t=0}^{t=\infty} - \int_{t=0}^{t=\infty} \frac{-\exp(-at)}{a}\,\omega\,\cos(\omega t)\,\mathrm{d}t$$

$$\int_{t=0}^{t=\infty} \exp(-at)\sin(\omega t)\,\mathrm{d}t = [0-0] + \frac{\omega}{a}\int_{t=0}^{t=\infty} \exp(-at)\cos(\omega t)\,\mathrm{d}t$$

$$\int_{t=0}^{t=\infty} \exp(-at)\sin(\omega t)\,\mathrm{d}t = \frac{\omega}{a}\int_{t=0}^{t=\infty} \exp(-at)\cos(\omega t)\,\mathrm{d}t$$

We can now substitute for the sine integral (the second term on the right hand side) in the intermediate result (yellow high lighted) above.

$$\int_{t=0}^{t=\infty} \cos(\omega t)\exp(-at)\,\mathrm{d}t = \frac{1}{a} - \frac{\omega}{a}\left(\frac{\omega}{a}\int_{t=0}^{t=\infty} \exp(-at)\cos(\omega t)\,\mathrm{d}t\right)$$

$$\int_{t=0}^{t=\infty} \cos(\omega t)\exp(-at)\,\mathrm{d}t = \frac{1}{a} - \frac{\omega^2}{a^2}\int_{t=0}^{t=\infty} \exp(-at)\cos(\omega t)\,\mathrm{d}t$$

Taking the integral from the right hand side over to the left hand

$$\left(1+\frac{\omega^2}{a^2}\right)\int_{t=0}^{t=\infty} \cos(\omega t)\exp(-at)\,\mathrm{d}t = \frac{1}{a}$$

$$\frac{a^2+\omega^2}{a^2}\int_{t=0}^{t=\infty} \cos(\omega t)\exp(-at)\,\mathrm{d}t = \frac{1}{a}$$

$$\int_{t=0}^{t=\infty} \cos(\omega t)\exp(-at)\,\mathrm{d}t = \frac{a}{a^2+\omega^2}$$

Thus the Fourier transform of our simple exponential time domain decay function,

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

may be transformed into the frequency domain signal which is required for chemical interpretation using the simple equation shown below. Remembering to insert √(2/π) we have,

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

Figs.5.5 shows the time domain signal for a simple exponential decay of the sort we have been considering. Fig. 5.6 shows the intensity versus frequency domain spectrum after the Fourier transform for this decay signal.

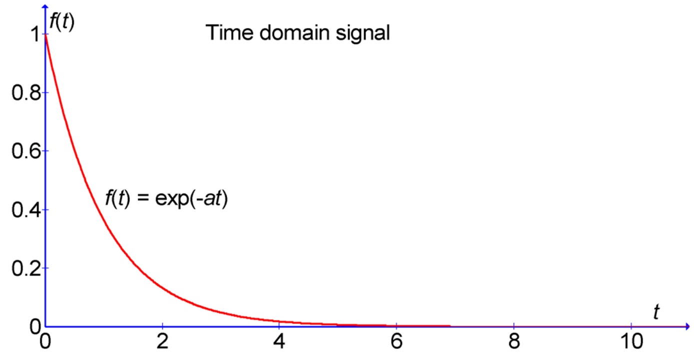


Figure 5.5: Free Induction Decay (FID), Total Signal Intensity Versus Time.

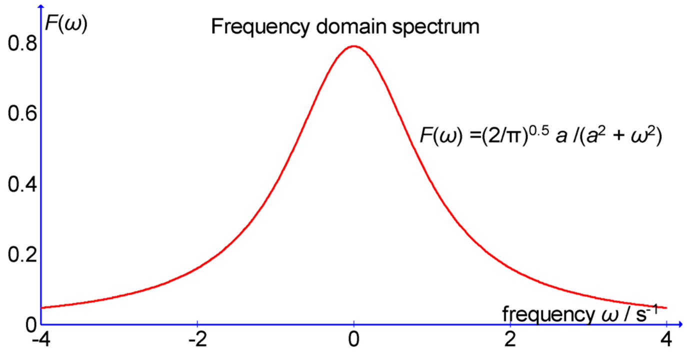


Figure 5.6: Fourier Transformed Frequency Domain Spectrum, Intensity Versus Frequency.

Clearly in a real spectrum there would be many peaks each with their own intensity and the free induction decay would be very complex. The spectrometers that chemists commonly use have computer software which applies the above technique to the FID to obtain the "normal" or frequency spectrum.

Return to Question 5 (see page 60)

5.2.6 Solution 6: Integrated Rate Law for a 2nd order Reaction with Two Reactants

So that we can calculate the integral in the equation

$$\int_0^x \frac{1}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)}\,\mathrm{d}x = kt$$

we require the fractional product on the left hand side to be expressed as two separate fractions, that is we have to use partial fractions (see Parker 2011, section 1.3.8) *before* we can integrate the equation. We write the identity function,

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

Don’t confuse the variables A and B (in italics and as yet unknown) and the chemical labels A and B (written in roman type). The identity, ≡, is true for *all* values of x whereas an equation is only true for certain values of x, called the solutions or roots of the equation. Bringing the two terms on the right of the identity to a common denominator gives,

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

To find the value of A we know that the identity is true for $x = [\mathrm{A}]_0$ which makes the second term in the right hand numerator zero. Thus the two numerators would become for $x = [\mathrm{A}]_0$

$$1 = A\left([\mathrm{B}]_0 - [\mathrm{A}]_0\right) + B\left([\mathrm{A}]_0 - [\mathrm{A}]_0\right)$$

$$A = \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}$$

The identity is also true for $x = [\mathrm{B}]_0$. Thus the two numerators would now become for $x = [\mathrm{B}]_0$

$$1 = A\left([\mathrm{B}]_0 - [\mathrm{B}]_0\right) + B\left([\mathrm{A}]_0 - [\mathrm{B}]_0\right)$$

$$B = \frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} = -A$$

Substituting the *now* known values for A and B allows the partial fraction to be evaluated,

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

Taking common term $([\mathrm{B}]_0 - [\mathrm{A}]_0)$ outside a brackets gives,

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

These partial fractions allow us to now evaluate the integral for our second-order chemical kinetics problem.

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

$$\int_0^x \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\left(\frac{1}{[\mathrm{A}]_0 - x} - \frac{1}{[\mathrm{B}]_0 - x}\right)\mathrm{d}x = kt$$

Taking the constant term outside the integral for clarity,

$$\frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\int_0^x \left(\frac{1}{[\mathrm{A}]_0 - x} - \frac{1}{[\mathrm{B}]_0 - x}\right)\mathrm{d}x = kt$$

$$\frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\left[-\ln\left([\mathrm{A}]_0 - x\right) + \ln\left([\mathrm{B}]_0 - x\right)\right]_0^x = kt$$

$$\frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\left(-\ln\left([\mathrm{A}]_0 - x\right) + \ln\left([\mathrm{B}]_0 - x\right) + \ln[\mathrm{A}]_0 - \ln[\mathrm{B}]_0\right) = kt$$

$$\frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\ln\frac{[\mathrm{A}]_0\left([\mathrm{B}]_0 - x\right)}{[\mathrm{B}]_0\left([\mathrm{A}]_0 - x\right)} = kt$$

Evidence in support that our chemical reaction follows this second-order rate law for two reactants,

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

comes from the plot shown in Fig. 5.7 where a straight line graph is supporting evidence and the gradient allows the rate constant k to be measured.

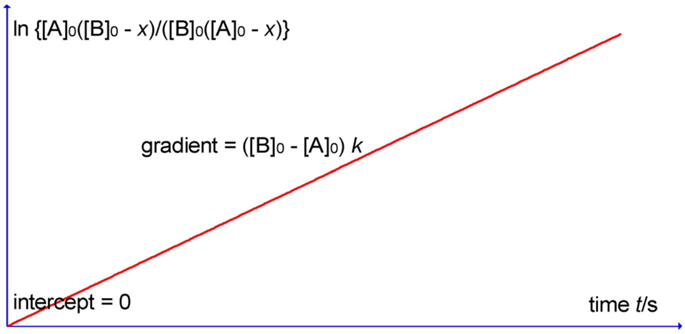


Figure 5.7: Integrated Rate Law Plot for Second-order Reaction with Two Reactants.

Return to Question 6 (see page 61)

6 Week 6: Chemical Applications of Integration

This week's tutorials covers four topics: (1) area under a curve, (2) average value of a function, (3) 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 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. If you repeat these heat capacity measurements at a series of different temperatures then we can convert from heat capacity to entropy by the following method.

Bismuth is a metal used in medicine, as an alloy for thermocouples, a nuclear reactor carrier for uranium, and in cosmetics. Bismuth's heat capacity slowly increases with temperature, see Table 6.1.

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 C_p/T against T, which in Maths is the integral of the curve between the two values of the x-axis.

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

Fig. 6.1 shows the plot for our data.

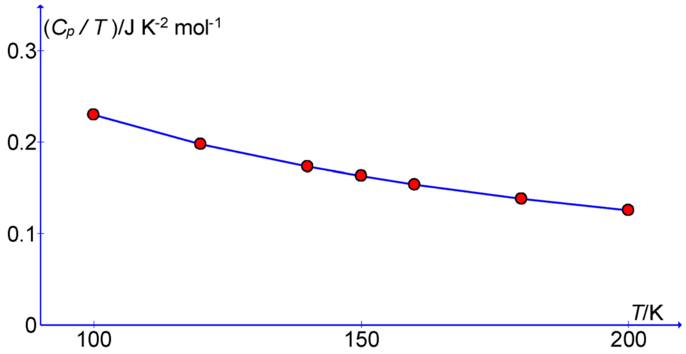


Figure 6.1: C_p/T versus T for Bismuth Metal.

Using our graphing spreadsheet the following third-order polynomial equation fits the curve from 100 to 200 K (but must *not* be extrapolated beyond that range). For clarity I have not included the units in this equation.

$$\frac{C_p}{T} = +0.5505 - 4.932\times 10^{-3}T + 2.050\times 10^{-5}T^2 - 3.229\times 10^{-8}T^3$$

Using integration find the entropy change for bismuth in heating the metal from 100 to 200 K.

Jump to Solution 1 (see page 81)

6.1.2 Question 2: The Average Distance from the Nucleus of an Electron in an Orbital

A second application of integration in chemistry is in the evaluation of the mean, or average, value of a quantity that changes continuously. Questions 2 and 3 are two examples in this use of integration.

The wavefunction ψ_{1s} of an electron in the $1s$ orbital of a hydrogen atom is

$$\psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} \exp\left(-\frac{r}{a_0}\right)$$

where a_o is the Bohr radius, equal to 0.5292 Å (Å is an angstrom = 10^{-10} m). The 1*s* atomic orbital is spherically symmetric, it only depends on the distance from the nucleus, *r*, and not on the angles of the polar coordinates. For a spherically symmetric orbital the *average* distance of the electron from the nucleus, symbol *r* pronounced "r bar" (averages are may also be written as <*r*> in some text books), is given by the integral,

$$\bar{r} = \int_{r=0}^{r=\infty} 4\pi r^3 (\psi_{1s})^2 \, \mathrm{d}r$$

Substituting the radial wavefunction into the above integral (remembering that $(e^x)^2 = e^{2x}$) gives us the integral we have to solve to find the average value of the distance of an electron from the nucleus for a 1*s* orbital. We will need to integrate by parts *three* times because of the r^3 term,

$$\bar{r} = \frac{4}{a_0^3} \int_{r=0}^{r=\infty} r^3 \exp\left(-\frac{2r}{a_0}\right) \mathrm{d}r$$

Jump to Solution 2 (see page 83)

6.1.3 Question 3: The Average Kinetic Energy of Gas Molecules

In the kinetic theory of gases, the probability that a molecule of mass *m* at temperature *T* will have a speed in the *x* direction between v_x and $v_x + \mathrm{d}v_x$ is given by the Maxwell-Boltzmann speed distribution.

$$f(v_x)\,\mathrm{d}v_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m v_x^2}{2 k_B T}\right) \mathrm{d}v_x$$

where k_B is Boltzmann's constant. The average *kinetic energy* in the *x* direction, T_x pronounced "T ex bar", is obtained by evaluating the integral,

$$\bar{T}_x = \int_{v_x=-\infty}^{v_x=+\infty} \frac{1}{2} m v_x^2 \, f(v_x) \, \mathrm{d}v_x$$

that is the integral below has to be solved,

$$\bar{T}_x = \int_{v_x=-\infty}^{v_x=+\infty} \frac{1}{2} m v_x^2 \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m v_x^2}{2 k_B T}\right) \mathrm{d}v_x$$

Obtain an expression for the average kinetic energy of gas molecules in the *x* direction by solving the above integral by making use of the substitution,

$$u = \left(\frac{m}{2 k_B T}\right)^{1/2} v_x$$

and using the standard integral,

$$\int_{x=-\infty}^{x=+\infty} x^{2} \exp\left(-x^{2}\right) \mathrm{d}\,x = \frac{1}{2}\sqrt{\pi}$$

Jump to Solution 3 (see page 85)

6.1.4 Question 4: Trapezium Rule Integration of C_p Data to Calculate Entropy

Obtaining thermodynamic functions, such as the entropy, from experimental measurements often requires integrating a function numerically. 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.

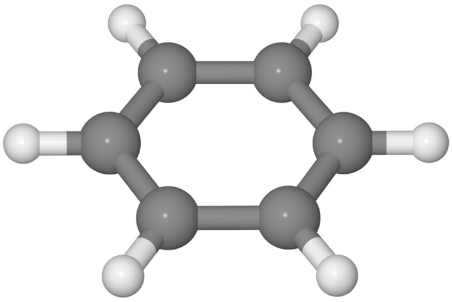


Figure 6.2: Benzene Molecule. C = dark grey, H = grey.

Benzene, Fig. 6.2, freezes below 5.5°C. A research student's experimental heat capacity data (with experimental scatter) for solid benzene is reported in Table 6.2 at several temperatures up to 273 K

T/K	23	48	73	123	173	223	273
C_p/J K^{-1} mol^{-1}	13.01	29.66	40.46	55.44	74.06	97.61	122.3
(C_p/T)/J K^{-2} mol^{-1}	0.57	0.62	0.55	0.45	0.43	0.44	0.45

Table 6.2: Solid Benzene Heat Capacity Data.

Assume that the heat capacity between 0 and 23 K is given by the Debye T^3 law which is,

$$C_p = a\,T^3$$

where a is a constant. Use the tabulated C_p value at 23 K to evaluate the constant, a, and then use an analytical integration from 0 to 23 K to find the entropy contribution from 0 to 23 K.

To determine the entropy contribution from 23 to 272 K use the relationship,

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

from the tabulated values of (C_p/T) against T apply the trapezium rule to numerically integrate from 23 to 273 K. The total entropy S of solid benzene at 273 K is then the sum of the two contributions 0-23 and 23-273 K.

Jump to Solution 4 (see page 86)

6.1.5 Question 5: Integral as a Length of a Curve, Entropy from Heat Capacity

As seen in Question 4, the evaluation of the change in entropy when a thermodynamic system varies from a state with temperature T_1 to a state with temperature T_2 can be made through integration of experimental heat capacity data. The determination of the change in entropy, ΔS between T_1 and T_2, then the integral can be thought of as a length of a curve,

$$\Delta S = \int_{S_1}^{S_2} \mathrm{d}S = \int_{T_1}^{T_2} \frac{C_p}{T}\, \mathrm{d}T$$

The heat capacity data of solid benzene reported in the Table 6.2 in Question 4 can be fitted using a polynomial, see Fig. 6.3. The blue curve is a fourth-order polynomial fitted between 23 to 273 K.

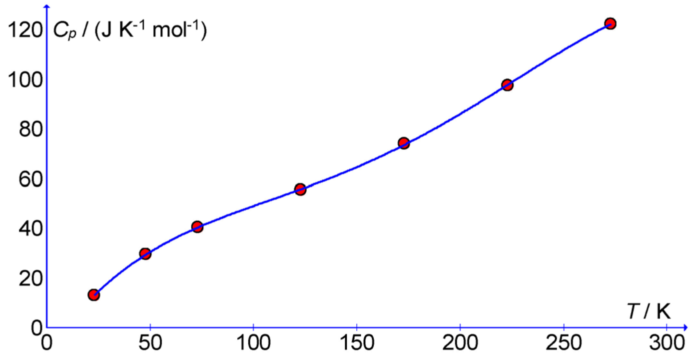


Figure 6.3: Solid Benzene Heat Capacity.

The data are reasonably accurately represented by the polynomial over the 23-273 K range. For clarity I have not included the units in this equation.

$$C_p = -9.792 + 1.202\,T - 1.002 \times 10^{-2}\,T^2 + 4.566 \times 10^{-5}\,T^3 - 6.807 \times 10^{-8}\,T^4$$

A polynomial is very useful as it is a curve which fits the data over a given range of values but it does *not* give us any new chemical insight. However, polynomials functions are easy to integrate and 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.

Determine the *change* in entropy, $\Delta S_{(23\text{-}273\ \mathrm{K})}$ when solid benzene is heated from 23 to 273 K and compare this result to the numerical integration of Solution 4.

Jump to Solution 5 (see page 88)

6.2 Week 6 Tutorial Solutions

6.2.1 Solution 1: Entropy Measurement of Solid Bismuth

The area under the curve is shown in Fig. 6.4.

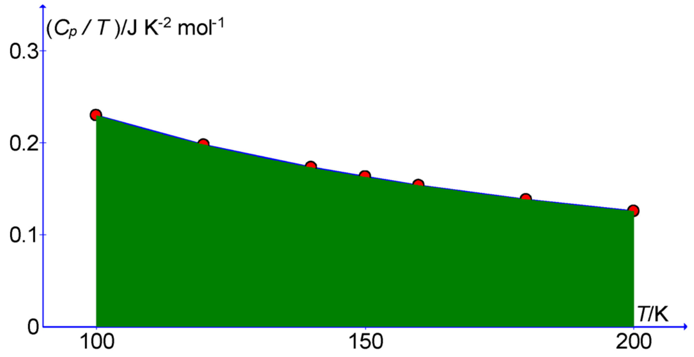


Figure 6.4: The Area Under the C_p/T versus T Curve for Solid Bismuth.

Using our polynomial fit to the data we can evaluate the integral (but ignoring units for clarity),

$$\Delta S_{(100-200\ \mathrm{K})} = \int_{T=100}^{T=200} (0.5505) - (4.932\times 10^{-3}\times T) + (2.050\times 10^{-5}\times T^{2}) - (3.229\times 10^{-8}\times T^{3})\,\mathrm{d}T$$

$$\Delta S_{(100-200\ \mathrm{K})} = \left[(0.5505\times T) - \frac{4.932\times 10^{-3}\times T^{2}}{2} + \frac{2.050\times 10^{-5}\times T^{3}}{3} - \frac{3.229\times 10^{-8}\times T^{4}}{4}\right]_{T=100}^{T=200}$$

The student's entropy change for solid bismuth between 100-200 K is,

$$\Delta S_{(100-200\ \mathrm{K})} = 16.79\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

Return to Question 1 (see page 76)

6.2.2 Solution 2: The Average Distance from the Nucleus of an Electron in an Orbital

$$\bar{r} = \frac{4}{a_0^3}\int_{r=0}^{r=\infty} r^3 \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r$$

It is possible to solve the integral through integration by parts

$$\int u\,\mathrm{d}v = uv - \int v\,\mathrm{d}u$$

with the substitutions below for u and dv and then differentiating u and integrating dv,

$$u = r^3 \qquad \frac{\mathrm{d}u}{\mathrm{d}r} = 3r^2 \qquad \mathrm{d}u = 3r^2\,\mathrm{d}r$$

$$\mathrm{d}v = \exp\left(-\frac{2r}{a_0}\right) \qquad \int \mathrm{d}v = \int \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r \qquad v = \frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)$$

Substituting u, du, dv and v back into the integration by parts equation gives,

$$\bar{r} = \frac{4}{a_0^3}\left(\left[r^3\frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)\right]_{r=0}^{r=\infty} - \int_{r=0}^{r=\infty}\frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)3r^2\,\mathrm{d}r\right)$$

From the shape of the negative exponential curve (Fig. 1.2), the exponential function tends faster to zero than r, r^2 and r^3 tend to infinity, and inserting the limits for the uv part of the integration by parts gives,

$$\bar{r} = \frac{4}{a_0^3}\left([0-0] - \int_{r=0}^{r=\infty}\frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)3r^2\,\mathrm{d}r\right)$$

$$\bar{r} = \frac{6}{a_0^2}\int_{r=0}^{r=\infty} r^2 \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r$$

This intermediate result can then be evaluated by applying once again integration by parts, after substituting,

$$u = r^2 \qquad \frac{\mathrm{d}u}{\mathrm{d}r} = 2r \qquad \mathrm{d}u = 2r\,\mathrm{d}r$$

$$\mathrm{d}v = \exp\left(-\frac{2r}{a_0}\right) \qquad \int \mathrm{d}v = \int \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r \qquad v = \frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)$$

$$\bar{r} = \frac{6}{a_0^2}\left(\left[r^2\frac{-a_0}{2}\exp\left(\frac{-2r}{a_0}\right)\right]_{r=0}^{r=\infty} - \int_{r=0}^{r=\infty}\frac{-a_0}{2}\exp\left(\frac{-2r}{a_0}\right)2r\,\mathrm{d}r\right)$$

Applying the limits of *r* gives,

$$\bar{r} = \frac{6}{a_0^2}\left([0-0] + a_0\int_{r=0}^{r=\infty} r\exp\left(\frac{-2r}{a_0}\right)\mathrm{d}r\right)$$

$$\bar{r} = \frac{6}{a_0}\int_{r=0}^{r=\infty} r\exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r$$

This second intermediate result can then be evaluated by applying the third and final integration by parts, after substituting,

$$u = r \qquad \frac{\mathrm{d}u}{\mathrm{d}r} = 1 \qquad \mathrm{d}u = \mathrm{d}r$$

$$\mathrm{d}v = \exp\left(-\frac{2r}{a_0}\right) \qquad \int \mathrm{d}v = \int \exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r \qquad v = \frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)$$

$$\bar{r} = \frac{6}{a_0}\left(\left[r\frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)\right]_{r=0}^{r=\infty} - \int_{r=0}^{r=\infty}\frac{-a_0}{2}\exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r\right)$$

Applying the limits to the first term gives,

$$\bar{r} = \frac{6}{a_0}\left([0-0] + \frac{a_0}{2}\int_{r=0}^{r=\infty}\exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r\right) = 3\int_{r=0}^{r=\infty}\exp\left(-\frac{2r}{a_0}\right)\mathrm{d}r$$

The integral can be integrated to give,

$$\bar{r} = 3\left[\frac{-a_0}{2}\exp\left(\frac{-2r}{a_0}\right)\right]_{r=0}^{r=\infty} = 3\left[0 - \frac{-a_0}{2}\right]$$

$$\bar{r} = \frac{3}{2}a_0 = 0.7938\ \mathring{\mathrm{A}}$$

The Bohr radius a_0 is at the *maximum* of the H-atom 1*s* probability radial distribution function and is 0.5292 Å, but the *average* distance the electron is from the nucleus is 0.7938 Å because of the asymmetric shape of the distribution function as shown in Fig. 6.5. The average radial distance $\bar{r}$ is where there is equal probability, areas under the curve, of less than or greater than the value of $\bar{r}$.

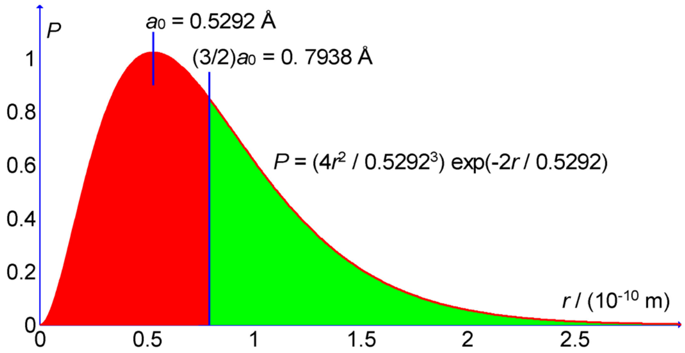


Figure 6.5: Hydrogen Atom 1*s* Radial Distribution Function.

Return to Question 2 (see page 77)

6.2.3 Solution 3: The Average Kinetic Energy of Gas Molecules

We can evaluate the integral,

$$\bar{T}_x = \int_{v_x=-\infty}^{v_x=+\infty} \frac{1}{2} m v_x^2 \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m v_x^2}{2 k_B T}\right) \mathrm{d} v_x$$

by using the suggested substituting for the constant terms and also squaring the substitution,

$$u = \left(\frac{m}{2k_\mathrm{B}T}\right)^{1/2} v_x \qquad u^2 = \frac{m v_x^2}{2k_\mathrm{B}T}$$

The exponential and the $\frac{1}{2}mv_x^2$ terms now become in our integral,

$$\bar{T}_x = \int_{v_x=-\infty}^{v_x=+\infty} k_\mathrm{B}T\,u^2 \left(\frac{m}{2\,\pi k_\mathrm{B}T}\right)^{1/2} \exp(-u^2)\,\mathrm{d}\,v_x$$

Cleaning this equation up gives,

$$\bar{T}_x = \frac{k_\mathrm{B}T}{\sqrt{\pi}} \int_{v_x=-\infty}^{v_x=+\infty} u^2 \left(\frac{m}{2k_\mathrm{B}T}\right)^{1/2} \exp\left(-u^2\right)\,\mathrm{d}\,v_x$$

Noting that the substitution does not alter the limits. Differentiating u,

$$\mathrm{d}\,u = \left(\frac{m}{2k_\mathrm{B}T}\right)^{1/2} \mathrm{d}\,v_x$$

Substituting into the average kinetic energy gives,

$$\bar{T}_x = \frac{k_\mathrm{B}T}{\sqrt{\pi}} \int_{u=-\infty}^{u=+\infty} u^2 \exp\left(-u^2\right)\,\mathrm{d}u$$

Using the standard integral suggested in Question 3,

$$\int_{x=-\infty}^{x=+\infty} x^2 \exp\left(-x^2\right)\,\mathrm{d}\,x = \frac{1}{2}\sqrt{\pi}$$

$$\boxed{\bar{T}_x = \frac{1}{2}k_\mathrm{B}T}$$

In Chemistry this is called the equipartition theorem.

Return to Question 3 (see page 78)

6.2.4 Solution 4: Trapezium Rule Integration of C_p Data to Calculate Entropy

To calculate the entropy, we make use of analytical integration up to 23 K and then numerical integration using the trapezium rule above 23 K,

$$S_{(0-23\,\mathrm{K})} = \int_{T=0}^{T=23} \frac{C_p}{T}\,\mathrm{d}\,T = \int_{T=0}^{T=23} \frac{a\,T^3}{T}\,\mathrm{d}\,T = \int_{T=0}^{T=23} a\,T^2\,\mathrm{d}\,T = \left[\frac{a\,T^3}{3}\right]_{T=0}^{T=23}$$

$$S_{(0-23\text{ K})} = a \times 4.056 \times 10^3\ \text{K}^3$$

The constant a is determined by using the measured heat capacity at 23 K, which is $C_p = 13.01$ J K^{-1} mol^{-1},

$$C_p = aT^3 \qquad a = \frac{13.01\ \text{J K}^{-1}\text{mol}^{-1}}{(23\ \text{K})^3} \qquad a = 1.069 \times 10^{-3}\ \text{J K}^{-4}\text{mol}^{-1}$$

The entropy contribution up to 23 K is,

$$S_{(0-23\text{ K})} = a \times 4.056 \times 10^3\ \text{K}^3 = \left(1.069 \times 10^{-3}\ \text{J K}^{-4}\ \text{mol}^{-1}\right)\left(4.056 \times 10^3 \text{K}^3\right)$$

$$\Delta S_{(0-23\text{ K})} = 4.336\ \text{J K}^{-1}\text{mol}^{-1}$$

The entropy contribution from above 23 K is determined using the trapezium rule. Fig. 6.6 shows that the area under the blue curve between the limits of a particular "slice" is approximated by the sum of the areas of the rectangle and the triangle. The approximation becomes better the narrower we make the slice (*i.e.* the more data points we can measure), we then add the contributions from several slices to obtain the approximate area between wider limits.

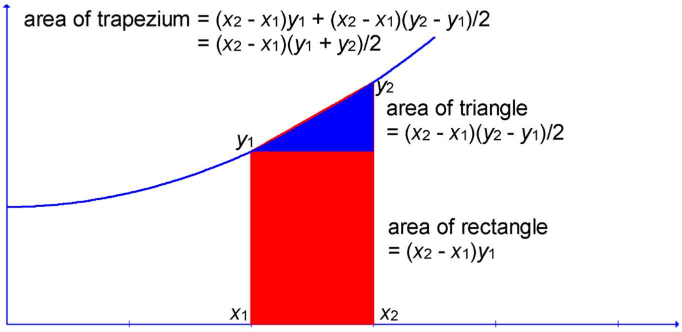


Figure 6.6: The Trapezium Rule.

The area of a trapezium is given below and derived in Fig. 6.6.

$$\text{Area} = \frac{(x_2 - x_1)(y_1 + y_2)}{2}$$

Always draw a graph of the data to check whether you have made a simple error in processing the raw data or if there is a "rogue" experimental point which should either be ignored or remeasured. Our heat capacity data from Table 6.3 is plotted in Fig. 6.7 as C_p/T against T. The advantage of the trapezium rule is that it ideal for spreadsheet evaluation.

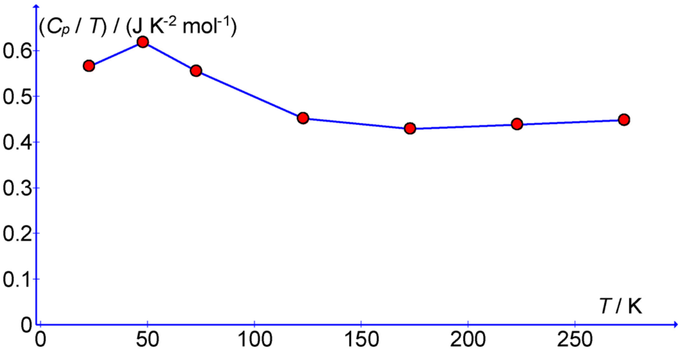


Figure 6.7: Graph of (C_p /T) agains

T/K	23	48	73	123	173	223	273
C_p/J K^{-1} mol^{-1}	13.01	29.66	40.46	55.44	74.06	97.61	122.30
(C_p/T)/J K^{-2} mol^{-1}	0.5657	0.6179	0.5542	0.4507	0.4281	0.4377	0.4480
$(x_2 - x_1)$		25	25	50	50	50	50
$(y_1 + y_2)/2$		0.5887	0.5861	0.5025	0.4394	0.4329	0.4429
$(x_2 - x_1)(y_1 + y_2)/2$		14.72	14.65	25.13	21.97	21.65	22.15

Table 6.3: Benzene Heat Capacity Data from 23 K to 273 K.

The sum of the areas is,

$$\Delta S_{(23-273\text{ K})} = 120.3\text{ J K}^{-1}\text{mol}^{-1}$$

The total entropy of solid benzene at 273 K (0°C) is the sum of the contributions from 0-23 K and 23-273 K.

$$S_{273\text{ K}} = 124.6\text{ J K}^{-1}\text{mol}^{-1}$$

Return to Question 4 (see page 79)

6.2.5 Solution 5: Integral as a Length of a Curve, Entropy from Heat Capacity

The change in entropy is obtained by evaluating the integral,

$$\Delta S = \int_{S_1}^{S_2} \mathrm{d}S = \int_{T=23}^{T=273} \frac{C_p}{T}\,\mathrm{d}T$$

$$\Delta S_{(23-273\text{ K})} = \int_{T=23}^{T=273} -\frac{9.792}{T} + 1.202 - 1.002\times10^{-2}T + 4.566\times10^{-5}T^2 - 6.807\times10^{-8}T^3\,\mathrm{d}T$$

$$\Delta S_{(23-273\ \mathrm{K})} = \left[-9.792\ln(T) + 1.202T - \frac{1.002\times 10^{-2}T^{2}}{2} + \frac{4.566\times 10^{-5}T^{3}}{3} - \frac{6.807\times 10^{-8}T^{4}}{4}\right]_{T=23}^{T=273}$$

Substituting in the integration limits and displaying the equation over several lines for clarity we have,

$$\begin{aligned}\Delta S_{(23-273\ \mathrm{K})} = &\left[-9.792\ln(273) + 1.202\times 273 - \frac{1.002\times 10^{-2}\times 273^{2}}{2}\right]\\ &+\left[+\frac{4.566\times 10^{-5}\times 273^{3}}{3} - \frac{6.807\times 10^{-8}\times 273^{4}}{4}\right]\\ &-\left[-9.792\ln(23) + 1.202\times 23 - \frac{1.002\times 10^{-2}\times 23^{2}}{2}\right]\\ &-\left[+\frac{4.566\times 10^{-5}\times 23^{3}}{3} - \frac{6.807\times 10^{-8}\times 23^{4}}{4}\right]\end{aligned}$$

$$\begin{aligned}\Delta S_{(23-273\mathrm{K})} = &-9.792\ln\left(\frac{273}{23}\right) + 1.202\times(273-23) - \frac{1.002\times 10^{-2}\times(273^{2}-23^{2})}{2}\\ &+\frac{4.566\times 10^{-5}\times(273^{3}-23^{3})}{3} - \frac{6.807\times 10^{-8}\times(274^{4}-23^{4})}{4}\end{aligned}$$

$$\Delta S_{(23-273\ \mathrm{K})} = -24.23 + 300.5 - 370.7 + 309.5 - 94.52$$

$$\Delta S_{(23-273\ \mathrm{K})} = 120.6\ \mathrm{J\ K^{-1}mol^{-1}}$$

In Question 4 the numerical integration (trapezium rule) gave $\Delta S_{(23\text{-}273)\ \mathrm{K}} = 120.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$ so the two methods agree to ±0.3 in 120 or ~0.3% which is pretty good. In this case the numerical trapezium rule had rather wide strips and hence would be expected to be less precise than the integral length of a curve method.

Return to Question 5 (see page 80)

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. Firstly, we consider how each data point varies from the mean of the data $\bar{y}$ (pronounced "y bar"). We calculate $(y_i - \bar{y})$ which is called the *residual* R of an individual data point and is the deviation of a given data y_i point from the mean of the measurements, $\bar{y}$.

$$R = \left(y_i - \bar{y}\right)$$

Squaring the residual 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*.

$$SR = \left(y_i - \bar{y}\right)^2$$

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

$$SSR = \sum_{i=1}^{n} \left(y_i - \bar{y}\right)^2$$

The standard deviation of all the n data points is defined as,

$$\sigma_y = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left(y_i - \bar{y}\right)^2}$$

$$\sigma_y = \sqrt{\frac{1}{n-1} SSR}$$

Often in Chemistry the result of a given experiment is calculated from one or more set of independent experimental measurements. The standard deviation of the result has to be computed from the known (or estimated) standard deviations of each variable using the error propagation formula. If the calculated quantity y is a function of a, b, c, …, that is,

$$y = f(a, b, c, \ldots)$$

The square of the standard deviation σ_y^2 (called the variance) is related to the variances of the variables (a, b, c) and is given by the error propagation formula,

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

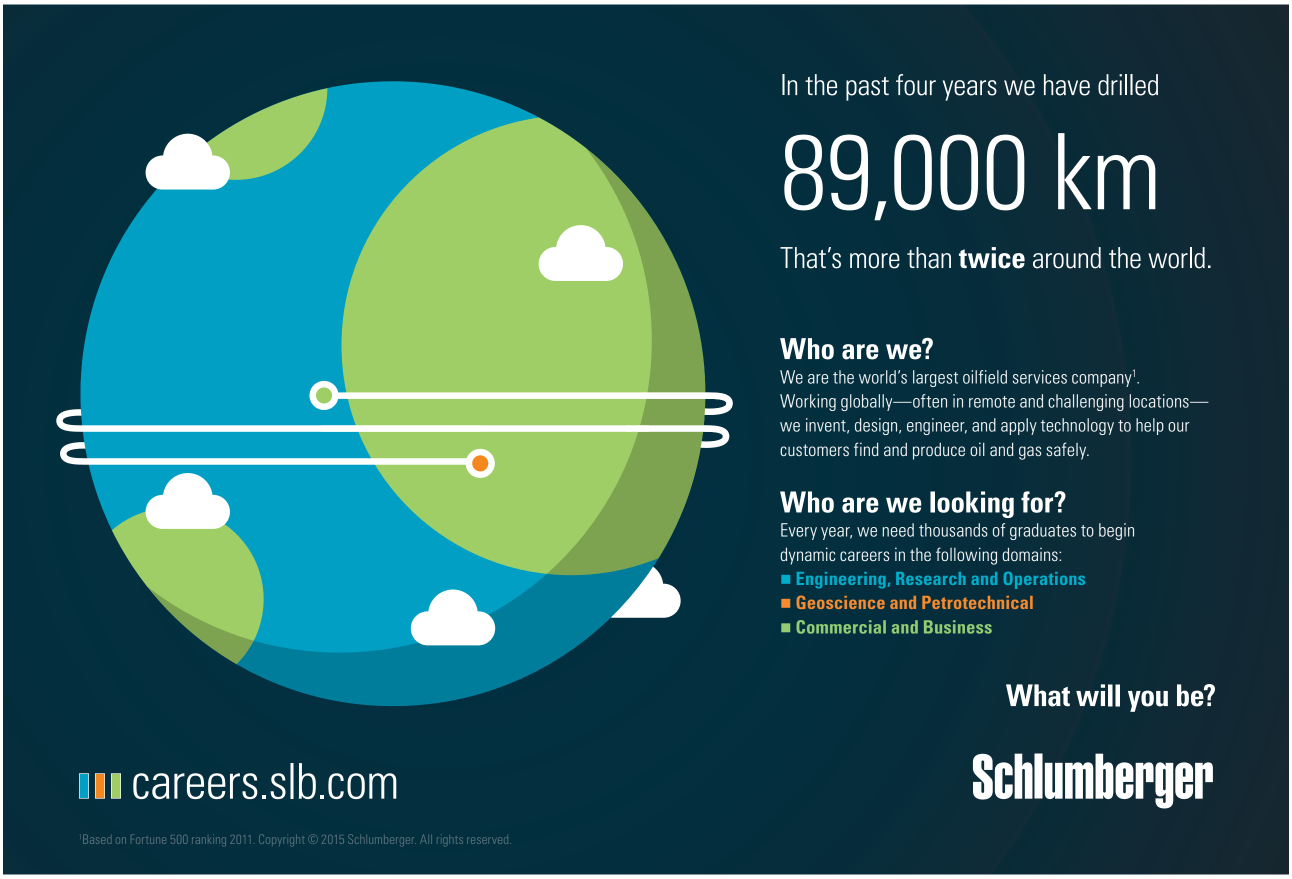
Where $\partial y/\partial a$ (pronounced "del y by del a") means the partial derivative, that is the differential of y with respect to a but treating the other variables b, c, *etc.* as constants for *this* partial derivative. The other partial derivatives are treated in an equivalent fashions.

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 of workbooks (Parker 2013) which begins with linear and nonlinear curve fitting of experimental data.

7.1 Week 7 Tutorial Questions

7.1.1 Question 1: Analysis of Traces 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 quality, food and in blood analysis. In scientific archaeology and forensic science the composition of trace elements of artefacts made from metal, pottery, or glass, gives information on their origins and ages. Fig. 7.1 shows a schematic diagram of the AAS instrument which you may use in your lab classes.



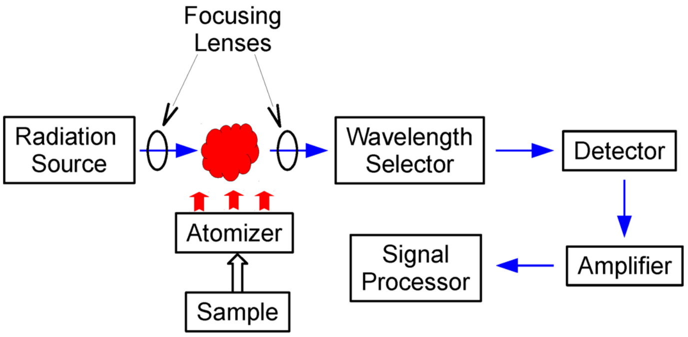


Figure 7.1: Schematic AAS Instrument.

The atomizer is commonly a high temperature flame, or a hot graphite tube. Atoms absorb at specific wavelengths due to their quantum mechanics and hence the absorption at the chosen wavelength leads to a measure of the absorbance of that wavelength and eventually the Chemist can use the absorbance value to calculate the concentration of the atom.

Chromium(VI) is one element which is known to be 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. Absorbance values, which are pure numbers, obtained for Cr(VI) solutions using the chromium resonance line at λ = 357.9 nm are reported below. Three different samples of water were taken and measured by AAS and each sample was measured three separate times, see Table 7.1.

Sample	Run 1	Run 2	Run 3
1	0.254	0.253	0.254
2	0.253	0.254	0.253
3	0.248	0.247	0.248

Table 7.1: Absorbance Values for AAS Analysis for Cr(VI) at λ = 357.9 nm.

Determine the average absorbance of all nine measurements, the standard deviation and then the relative standard deviation (defined as the standard deviation divided by the average value, σ_y / y).

Jump to Solution 1 (see page 95)

7.1.2 Question 2: Solubility Product and Error Propagation

Silver chloride AgCl is a white solid which is only very slightly soluble in water,

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

The solubility product, K_S, is the equilibrium constant for the reaction of the solid dissolving in the solvent to its constituent ions.

$$K_S = \frac{\dfrac{[\mathrm{Ag}^+(\mathrm{aq})]}{c^o}\ \dfrac{[\mathrm{Cl}^-(\mathrm{aq})]}{c^o}}{\dfrac{[\mathrm{AgCl}\ (\mathrm{aq})]}{c^o}}$$

Where each concentration is divided by its standard state, c^o, which is 1 mol L^{-1} for the solute ions, hence the units cancel out for the solutes. The standard state for any *pure solid* (*e.g.* AgCl) or any *pure liquid*, is unity and so a pure solid or pure liquid do not appear in the solubility product (or in an equilibrium constant). 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. So conventionally the solubility product is written as,

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

but these are understood to be unit-less "concentrations" as the units have been cancelled out by division with the standard state. So a solubility product (or any equilibrium constant) is dimensionless. The solubility, *S*, has units of mol L^{-1} (as it is *not* divided by its standard state), and is defined as,

$$S = [\mathrm{Ag}^+(\mathrm{aq})] \text{ and } S = [\mathrm{Cl}^-(\mathrm{aq})]$$

Thus the solubility product for our AgCl saturated solution is written as $K_S = S^2$.

$$S = K_S^{1/2}$$

Using the error propagation formula determine the solubility *S*, the standard deviation σ_S and the relative standard deviation σ_S / S in the calculated value of the solubility *S* of silver chloride AgCl knowing that its solubility product is $K_s = (1.82 \pm 0.20)\times 10^{-10}$.

Jump to Solution 2 (see page 96)

7.1.3 Question 3: Wavefunctions and Probability

In quantum mechanics the particle in a box is used to model the translational motion of electrons, ions, atoms or molecules. We are going to use the model to estimate the transition energies in a conjugated molecule such as dye molecule. For example β-carotene is the red food pigment found in carrots and many other fruits and vegetables, see Fig. 7.2. It is red because of its conjugated double bond structure enables it to absorb at the blue end of the visible spectrum.

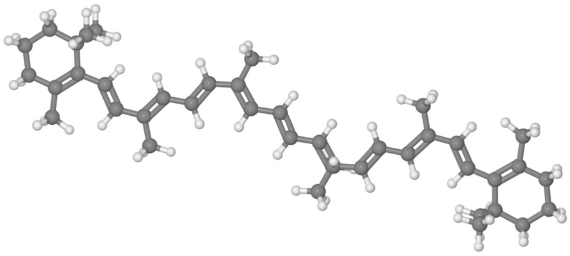


Figure 7.2: β-Carotene Molecule. H = grey, C = dark grey.

For a particle of mass m confined between two walls at $x = 0$ and $x = L$, the energy of the particle is quantized and may only have following set of values,

$$E = \frac{n^2 h^2}{8 m L^2}$$

The quantum number n (called the translational quantum number) may take the values $n = 1, 2, 3, \ldots$. The wavefunction of the trapped particle is,

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L}$$

where the angle is in *radians*. The probability P of finding the particle in a specified region is the integral of ψ_n^2 dx over that region of space.

Consider an electron confined to a molecule of length $L = 1.0$ nm (roughly five atoms long) and calculate the probability that when it is in the ground state ($n = 1$) the electron is found in the region between $x = 0$ and $x = 0.2$ nm.

Jump to Solution 3 (see page 97)

7.2 Week 7 Tutorial Solutions

7.2.1 Solution 1: Analysis of Traces by Atomic Absorption Spectroscopy

The average or mean of all 9 absorbances $\bar{y}$ is,

$$\bar{y} = 0.251555$$

I have deliberately used an excess number of significant figures at this intermediate stage so that later rounding errors are reduced. We will correct this situation later on in the solution.

I used a hand calculator to calculate the values of the square of the residuals, SR, are shown in Table 7.2. but obviously for larger data sets we would use a spreadsheet.

Sample	Run 1	Run 2	Run 3
1	5.9780×10^{-6}	2.0880×10^{-6}	5.9780×10^{-6}
2	2.0880×10^{-6}	5.9780×10^{-6}	2.0880×10^{-6}
3	1.2638×10^{-5}	2.0748×10^{-5}	1.2638×10^{-5}

Table 7.2: The Square of the Residuals, *SR*, for the AAS Absorbances.

The sum of these squares of the residuals is $SSR = 7.0222\times10^{-5}$ and thus the standard deviation is,

$$\sigma_y = \sqrt{\frac{1}{9-1}\left(7.0222\times10^{-5}\right)}$$

$$\sigma_y = 2.9627\times 10^{-3}$$

In your lab note book you would then quote your AAS measurements as,

$$\text{AAS absorbance of Cr(VI) present in water samples} = 0.252 \pm 0.003$$

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), *i.e.* the extinction coefficient at this wavelength, the analytical chemist would then calculate the concentration of the pollutant. As experimentalists, chemists are also interested in finding the *relative standard deviation*, that is comparing the standard deviation with the mean of the readings (*i.e.* how good is your experimental method and your equipment). The current reading are precise to about 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.

$$\text{Relative standard deviation} = \frac{0.003}{0.252} = 1.19\times 10^{-2} = 1.19\,\%$$

Return to Question 1 (see page 91)

7.2.2 Solution 2: Solubility Product and Error Propagation

Fig. 7.3 shows the crystal structure of solid silver chloride.

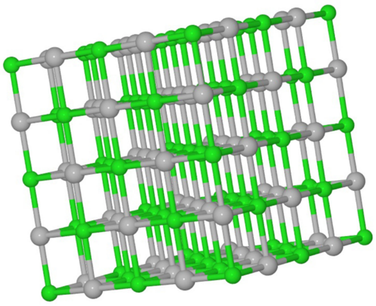


Figure 7.3: AgCl Crystal. Ag = grey, Cl = green.

The solubility is calculated from the square root of the solubility product.

$$S = K_S^{1/2} = \left(1.82\times 10^{-10}\right)^{1/2} = 1.3491\times 10^{-5}\ \text{mol L}^{-1}$$

Where I have deliberately retained extra decimal places for the moment to reduce later rounding errors. This will be corrected when we have its standard deviation. The error propagation formula for this simple *one* independent variable problem means that the partial derivatives become full derivatives. For this one-variable case we may then take the square roots on each side of the error propagation equation,

$$\sigma_S^2 = \left(\frac{\mathrm{d}\,S}{\mathrm{d}\,K_S}\right)^2 \sigma_{K_S}^2 \qquad \sigma_S = \left(\frac{\mathrm{d}\,S}{\mathrm{d}\,K_S}\right)\sigma_{K_S}$$

$$\sigma_S = \frac{1}{2} K_S^{-1/2}\,\sigma_{K_S} \qquad \sigma_S = \frac{0.02\times 10^{-10}\ \text{mol L}^{-1}}{2\left(1.82\times 10^{-10}\right)^{1/2}}$$

$$\sigma_S = 7.4125\times 10^{-8}\ \text{mol L}^{-1}$$

The solubility may now be quoted to the correct number of decimal places,

$$S = (1.349 \pm 0.007) \times 10^{-5}\ \text{mol L}^{-1}$$

The relative standard deviation is,

$$\frac{\sigma_S}{S} = \frac{7.4125 \times 10^{-8}\ \text{mol L}^{-1}}{1.349 \times 10^{-5}\ \text{mol L}^{-1}} = 5.4948 \times 10^{-3} \approx 0.55\%$$

The relative precision is 0.55% which is pretty good.

Return to Question 2 (see page 92)

7.2.3 Solution 3: Wavefunctions and Probability

The wavefunction of the electron in the ground state ($n = 1$) is given by,

$$\psi_1 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right)$$

The probability P in the region between $x = 0$ and $x = 0.2$ nm is found by evaluating the integral,

$$P = \int_{x=0}^{x=0.2} \psi_1^2 \, \mathrm{d}x = \frac{2}{L}\int_{x=0}^{x=0.2} \sin^2\left(\frac{\pi x}{L}\right)\mathrm{d}x$$

To evaluate the integral we make use of the trigonometric relationship,

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

$$P = \frac{2}{L}\int_{x=0}^{x=0.2} \frac{1}{2}\left(1 - \cos\left(\frac{2\pi x}{L}\right)\right)\mathrm{d}x \qquad P = \frac{1}{L}\left[x - \frac{L}{2\pi}\sin\left(\frac{2\pi x}{L}\right)\right]_{x=0}^{x=0.2}$$

$$P = \frac{1}{L}\left[0.2 - \frac{L}{2\pi}\sin\left(\frac{2\pi 0.2}{L}\right)\right] - \frac{1}{L}\left[0 - \frac{L}{2\pi}\sin\left(\frac{0}{L}\right)\right] \qquad P = \frac{0.2}{L} - \frac{1}{2\pi}\sin\left(\frac{0.4\pi}{L}\right)$$

For $L = 1$ nm the probability is as below, the angle being in *radians* not degrees,

$$P = 0.2 - \frac{1}{2\pi}\sin(0.4\pi) \qquad P = 0.2 - 0.1514$$

$$\boxed{P = 0.0486}$$

That is the probability is about 0.05 (or ~5% of the total probability) that the electron is between 0 and 0.2 nm. Fig. 7.4 shows the wavefunction squared and the shaded area is the probability that the electron is between 0 and 0.2 nm.

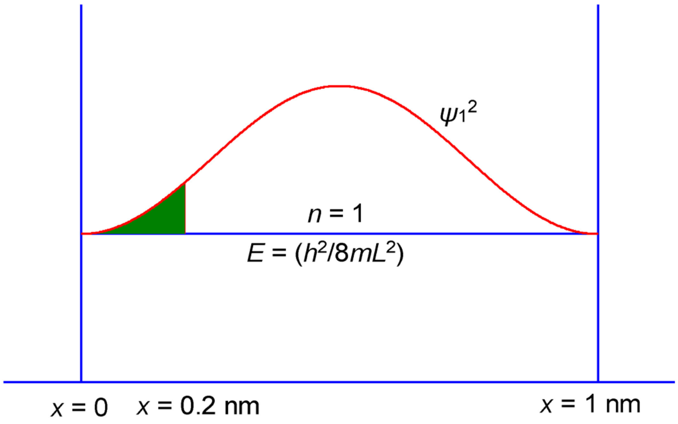


Figure 7.4: Wavefunction Squared for an Electron in a "Box" of Length = 1 nm.

Return to Question 3 (see page 93)

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 energy levels, that is their populations in the various quantum levels, Fig. 8.1. Don't confuse this quantum based Boltzmann distribution with the Maxwell-Boltzmann distribution which deals with the non-quantized (or classical) translational motion of molecules.

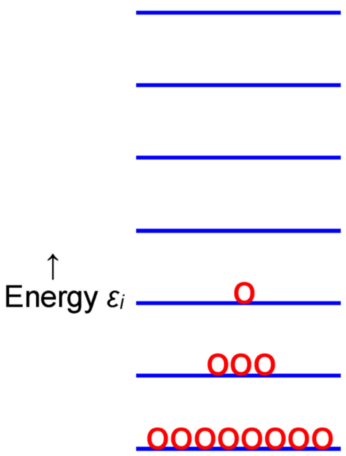


Figure 8.1: Schematic Population of Molecules in Energy Levels.

If N represents the total number of molecules, then the number of molecules n_i having energy ε_i with respect to the zero energy which is appropriate for that type of "motion", is given by,

$$\frac{n_i}{N} = \frac{\exp\left(-\dfrac{\varepsilon_i}{k_B T}\right)}{\sum_i \exp\left(-\dfrac{\varepsilon_i}{k_B T}\right)}$$

Where k_B is Boltzmann's constant and the summation is over all the allowed quantum 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 quantum levels i and j.

Jump to Solution 1 (see page 102)

8.1.2 Question 2: Populations of Molecules in Translational, Rotational, Vibrational and Electronic Energy Levels

Let us consider a hydrogen molecule, H_2, see Fig 8.2.

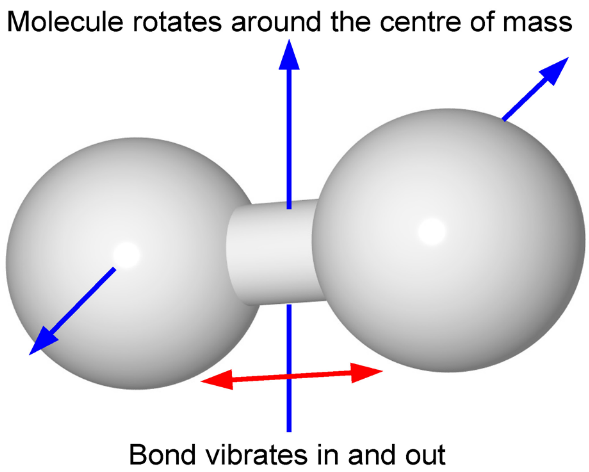


Figure 8.2: Hydrogen Molecule.

H_2 molecules can undergo translational motion (movement of the whole molecule through space); rotational motion (the molecule rotates around the centre of mass); vibrational motion (the bond length increases and decreases); and electronic energy level changes. The energy differences, $\Delta\varepsilon$, associated with the difference between the energies of the first excited (or upper level u), εu and the ground state ε_g, for translation, rotation, vibration and electronic energies are listed in Table 8.1. Note that I have quoted the energy in J molecule^{-1} although this is strictly a non-SI unit (it should be J) it is very useful in reminding us that it is the energy per molecul

Motion	ΔE/J molecule^{-1}
translation	4.918×10^{-41}
rotation	4.805×10^{-21}
vibration	8.2605×10^{-20}
electronic	1.8215×10^{-18}

Table 8.1: Energy Gaps for the H_2 Molecule.

H_2 molecules in the gas phase at room temperature, T = 298 K, 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. This may happen for each of the possible molecular motions listed in Table 8.1 and H_2 will quickly reach a thermodynamic equilibrium of populations characteristic of its temperature of 298 K.

Using these values for the energy gaps calculate the relative population n_u/n_g for the first excited state relative to the ground state, at room temperature T = 298 K, for each of the motions using *your derived equation* for the Boltzmann distribution of populations from Question 1. The Boltzmann constant is $k_B = 1.381\times10^{-23}$ J K^{-1}. (We are assuming no degeneracy of the levels, don't worry about this simplification about degeneracy as it will be discussed later on in your Chemistry course.)

Jump to Solution 2 (see page 102)

8.1.3 Question 3: Maxwell-Boltzmann Distribution of Molecules

Translational motion of molecules may be treated as a classical non-quantized motion. The Maxwell-Boltzmann distribution $f(v)$ gives the probability that a molecule of mass m at temperature T will have velocity in three dimensions between v and v+dv,

$$f(v)\,\mathrm{d}v = 4\pi\left(\frac{m}{2\,\pi k_B T}\right)^{3/2}\exp\left(-\frac{mc^2}{2\,k_B T}\right)v^2\,\mathrm{d}v$$

where k_B is Boltzmann's constant is $k_B = 1.381\times10^{-23}$ J K^{-1}. For argon gas (relative molar mass 39.95) which has a mass m = 6.636 10^{-26} kg, calculate the most probable speed, v_{mp}, at 800 K, using the relationship

$$v_{mp} = \sqrt{\frac{2\,k_B T}{m}}$$

Secondly, estimate the fraction and the number of molecules per unit volume which have velocities which exceed the most probable speed by up to 1% given that the total number of molecules per unit volume is 9.00´10^{24} molecules cm^{-3}. In this small *dv* range assume that $f(v)$ is constant.

Jump to Solution 3 (see page 105)

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 2 versions of the Boltzmann distribution with subscripts *i* and *j*.

$$\frac{n_i}{N} = \frac{\exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{\sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)} \qquad \frac{n_j}{N} = \frac{\exp\left(-\frac{\varepsilon_j}{k_B T}\right)}{\sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right)}$$

The sum over all quantum levels *i* and all quantum levels *j* are the same, all we were doing was using a different symbol for the counting the levels, thus

$$\sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right) = \sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right)$$

We then take the ratio of n_i and n_j.

$$\frac{n_i N}{n_j N} = \frac{\exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{\exp\left(-\frac{\varepsilon_j}{k_B T}\right)}$$

The *N*s cancel out and to simplify the expression further we use the power relationship, $\exp(x)/\exp(y) = \exp(x - y)$.

$$\boxed{\frac{n_i}{n_j} = \exp\left(-\frac{\varepsilon_i - \varepsilon_j}{k_B T}\right)}$$

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

Return to Question 1 (see page 99)

8.2.2 Solution 2: Populations of Molecules in Translational, Rotational, Vibrational and Electronic Energy Levels

We use of the Boltzmann distribution equation derived in Solution 1,

$$\frac{n_i}{n_j} = \exp\left(-\frac{\varepsilon_i - \varepsilon_j}{k_B T}\right)$$

The relative population is determined by substituting $\Delta\varepsilon$ values, T and $k_B = 1.381\times10^{-23}$ J K^{-1} in the above equation for the Boltzmann distribution.

Motion	ΔE/J molecule^{-1}
translation	4.918×10^{-41}
rotation	4.805×10^{-21}
vibration	8.2605×10^{-20}
electronic	1.8215×10^{-18}

Table 8.2: H_2 Typical Energy Gaps for Various Molecular Motions.

Fig. 8.3 shows a schematic view of the various energy levels in a typical diatomic molecule with the spacing of the rotational levels J not to scale..

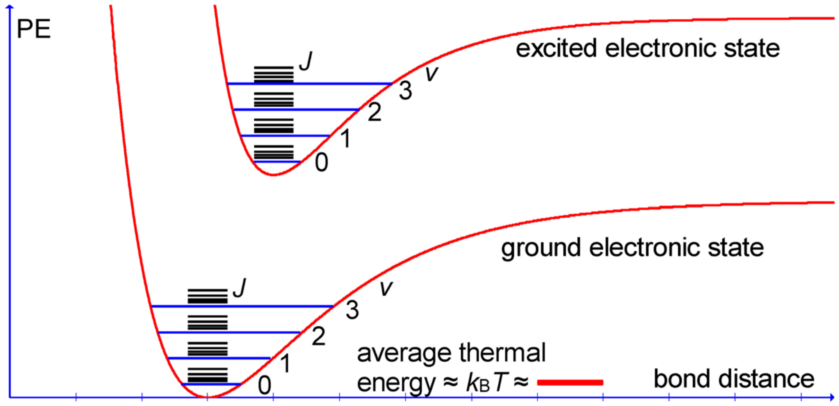


Figure 8.3: Schematic Energy Levels for a Typical Diatomic Molecule.

For translational motion we obtain,

$$\text{translational motion} \quad \frac{n_u}{n_g} = \exp\left(-\frac{4.918\times 10^{-41}\ \text{J}}{1.381\times 10^{-23}\ \text{J K}^{-1}\times 298\ \text{K}}\right) = 1$$

The energy gap for translational motion is negligibly small compared to the size of $k_BT = 4.115\times10^{-21}$ J at 298 K, which is a measure of the average thermal energy per molecule. There are, to a very good approximation, equal populations in the first excited and the ground translational energy levels. 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.

In fact the particle in a box energy gap is so small for molecules in macroscopic containers that we may very safely treat them classically, that is as if they are not quantized. This is the whole basis behind the Maxwell-Boltzmann distribution of translational velocities which we have met previously.

$$\text{rotational motion} \quad \frac{n_u}{n_g} = \exp\left(-\frac{4.805\times 10^{-21}\ \text{J}}{1.381\times 10^{-23}\ \text{J K}^{-1}\times 298\ \text{K}}\right) = 0.3111$$

The energy gap for the rotational motion of H_2 (the end-over-end rotation around the molecule's centre of mass, in this case the middle of the H–H bond) is similar to the average thermal energy. There are about 31 molecules in the excited rotational level for every 100 molecules in the ground rotational level.

$$\text{vibrational motion} \quad \frac{n_u}{n_g} = \exp\left(-\frac{8.2605\times 10^{-20}\ \text{J}}{1.381\times 10^{-23}\ \text{J K}^{-1}\times 298\ \text{K}}\right) = 1.917\times 10^{-9}$$

The H_2 bond vibrates in and out around its average equilibrium bond length and the energy gap to the excited vibrations level (which has a larger amplitude of vibrational motion) is ten times larger than the average thermal energy. A negligible fraction of H_2 molecules are in the excited vibrational level at 298 K, to a very good approximation all the H_2 molecules are in in their ground vibrational level at 298 K.

$$\text{electronic motion } \frac{n_u}{n_g} = \exp\left(-\frac{1.8215\times 10^{-18}\ \text{J}}{1.381\times 10^{-23}\ \text{J K}^{-1}\times 298\ \text{K}}\right) \approx 0$$

The thermal population of the first excited electronic state of H_2 is zero to a very *large* number of significant figures. This arises from the electronic gap being about 400 times larger than the average thermal energy for H_2. A similar situation occurs for most other molecules.

Return to Question 2 (see page 99)

8.2.3 Solution 3: Maxwell-Boltzmann Distribution of Molecules

The most probable speed is given by,

$$v_{\text{mp}} = \sqrt{\frac{2k_{\text{B}}T}{m}} \qquad v_{\text{mp}} = \sqrt{\frac{2\times 1.381\times 10^{-23}\ \text{J K}^{-1}\times 800\ \text{K}}{6.636\times 10^{-26}\ \text{kg}}}$$

$$v_{\text{mp}} = 577.0\ \text{m s}^{-1}$$

We have replaced the named unit joule by its fundamental units of J = kg $\text{m}^2\ \text{s}^{-2}$. The most probable speed of 577 m s^{-1} is an enormous speed and is typical of molecules. Remember, that molecules only travel on average short distances due to rapid collisions with other molecules about every 10^{-10} s.

Secondly, we are interested in calculating the fraction of molecules whose velocity ranges between 577.0 m s^{-1} and 577.0 + 5.77 = 582.8 m s^{-1} using the equation,

$$f(v)\,\text{d}v = 4\pi\left(\frac{m}{2\pi k_{\text{B}}T}\right)^{3/2}\exp\left(-\frac{mv^2}{2k_{\text{B}}T}\right)v^2\,\text{d}v$$

If $f(v)$ is assumed to be constant in the range v to v+dv we have the following (split over 2 lines for clarity).

$$\begin{aligned} f(v)\,\text{d}v = {} & 4\pi\left(\frac{6.636\times 10^{-26}\ \text{kg}}{2\pi\times 1.381\times 10^{-23}\ \text{J K}^{-1}\times 800\ \text{K}}\right)^{3/2} \\ & \times\exp\left(-\frac{6.636\times 10^{-26}\ \text{kg}\times\left(577.0\ \text{m s}^{-1}\right)^2}{2\times 1.381\times 10^{-23}\ \text{J K}^{-1}\times 800\ \text{K}}\right)\left(577.0\ \text{m s}^{-1}\right)^2\left(5.77\ \text{m s}^{-1}\right) \end{aligned}$$

$$f(v)\,\text{d}v = 4\pi\left(9.347\times 10^{-10}\ \text{m}^{-3}\text{s}^{3}\right)(0.3679)\left(1.921\times 10^{6}\ \text{m}^{3}\text{s}^{-3}\right)$$

$$f(v)\,\text{d}v = 8.301\times 10^{-3}$$

The fraction of molecules with velocity between 577.0 m s^{-1} and 582.8 m s^{-1} is $f(v)$ = 0.008301 or 0.83%. From this we can calculate the number of molecules by multiplying $f(v)$ by the total number of molecules N_{tot}.

$$f(v)\,\mathrm{d}v\,N_{\mathrm{tot}} = \left(8.301\times 10^{-3}\right)\left(9.00\times 10^{24}\ \text{molecules}\right)$$

$$\boxed{f(v)\,\mathrm{d}v\,N_{\mathrm{tot}} = 7.471\times 10^{22}\ \text{molecules}}$$

Molecules again is not an SI unit but it is a very useful reminder for us. Although the fraction of molecules is small the absolute number of molecules in this velocity range is enormous. Fig. 8.4 shows the area between the most probable velocity v_{mp} and v_{mp} + (0.01 v_{mp}) as a blue shaded area.

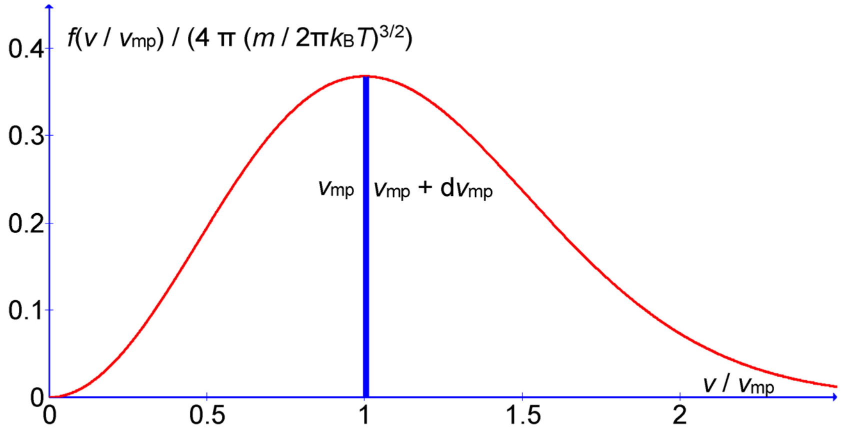


Figure 8.4: Maxwell-Boltzmann Speed Plot.

Return to Question 3 (see page 101)

Chemistry Maths 3 (Parker 2013) will continue to introduce the Maths tools that you as a first year Chemists, Chemical Engineers, Biochemists, Molecular Biologists, Biologists or Chemical Physicists will use in all the branches of your subject during the whole of your undergraduate studies and indeed in your later professional life.

8.3 References

Atkins, P & de Paula J 2009, *Atkins' Physical Chemistry*, 9th edn. Oxford University Press, Oxford.
Blackman, A Bottle, S Schmid, S Mocerino, M & Wille, U 2012, *Chemistry*, 2nd edn. John Wiley, Australia.
Parker, JE 2011, *Chemistry Maths 1*, BookBooN.com, Copenhagen.
Parker, JE 2012, *Chemistry Maths 2*, BookBooN.com, Copenhagen.
Parker, JE 2013, *Chemistry Maths 3*, BookBooN.com, Copenhagen.
Stroud, KA & Booth, DJ 2007, *Engineering Mathematics*, 6th edn. Palgrave MacMillan, Basingstoke.