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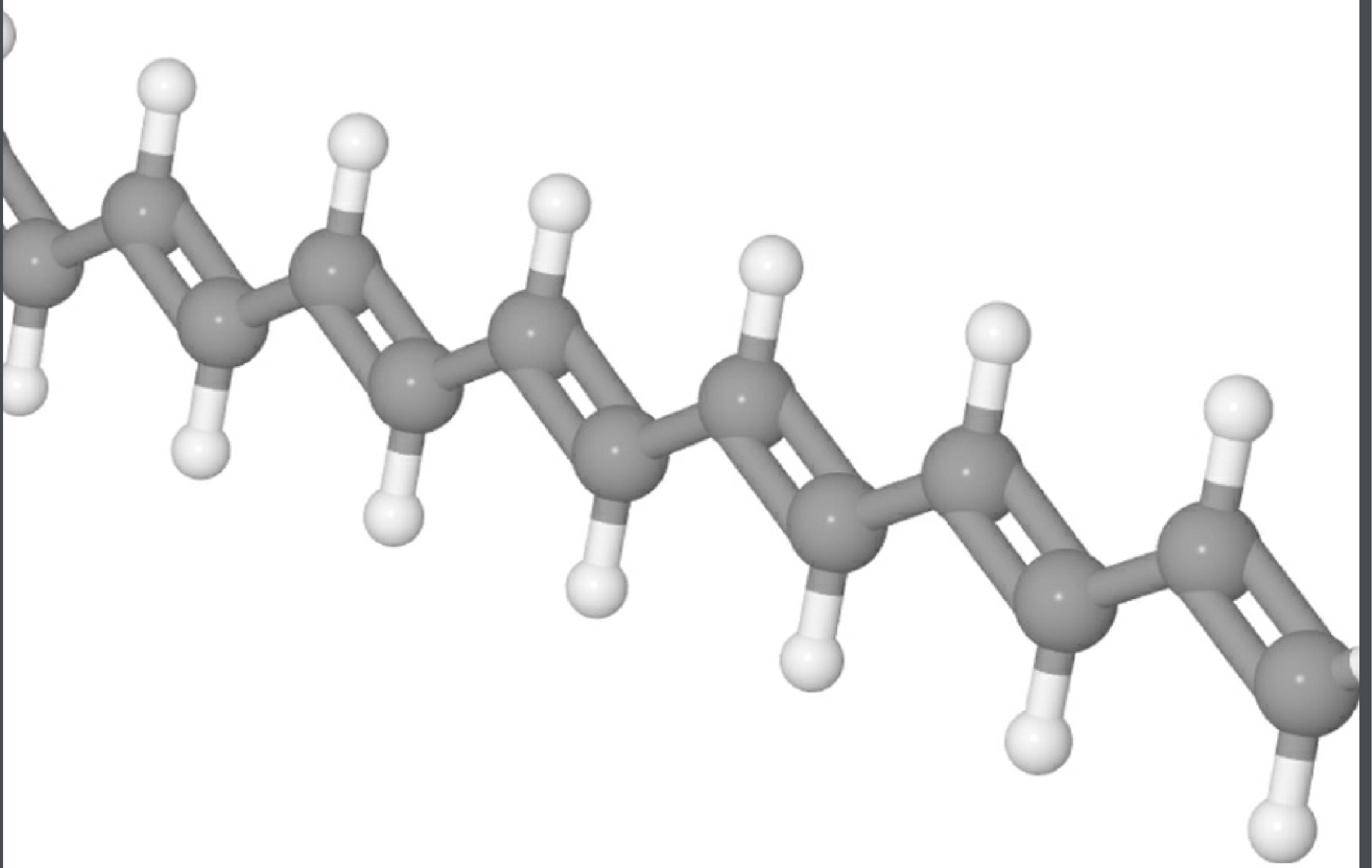
Introductory Maths for Chemists

Chemistry Maths 1

J. E. Parker



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Introductory Maths for Chemists

Chemistry Maths 1

2nd Edition

Introductory Maths for Chemists: Chemistry Maths 1
2nd edition

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Contents

Acknowledgements **7**

1 Week 1: Chemistry and Algebra 1 **8**
1.1 Introduction 8
1.2 Week 1 Tutorial Questions 14
1.3 Week 1 Tutorial Solutions 20

2 Week 2: Chemistry and Algebra 2 **29**
2.1 Week 2 Tutorial Questions 29
2.2 Week 2 Tutorial Solutions 41

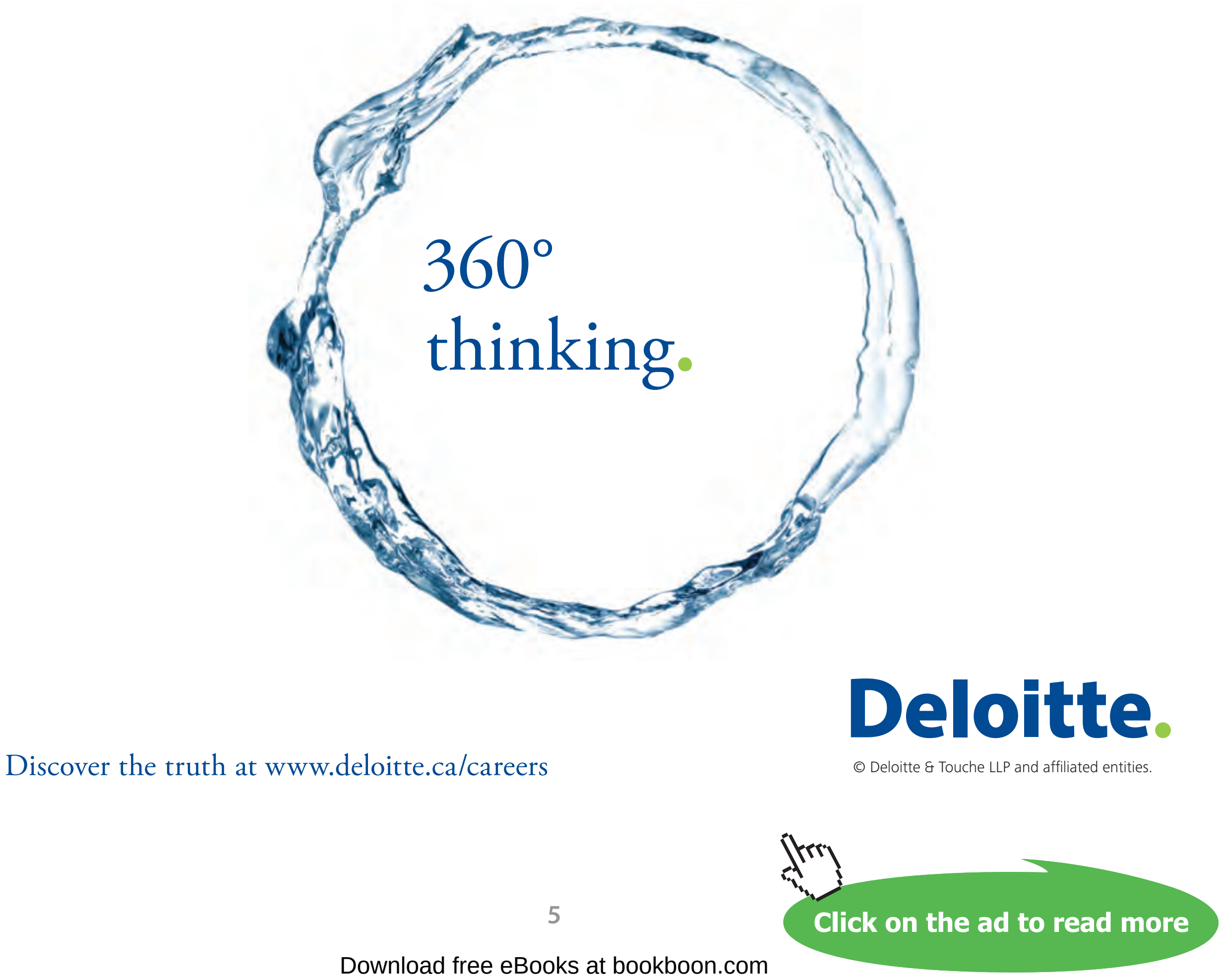
3 Week 3: Chemistry, Logarithms and Exponentials **54**
3.1 Summary of Logs, Exponentials, and Acid-Base Equilibrium 54
3.2 Week 3 Tutorial Questions 57
3.3 Week 3 Tutorial Solutions 64

4 Week 4: Experimental Data Analysis 74
4.1 Week 4 Tutorial Questions 74
4.2 Week 4 Tutorial Solutions 78

5 Week 5: Chemistry and Differentiation 1 85
5.1 Week 5 Tutorial Questions 85
5.2 Week 5 Tutorial Solutions 87

6 Week 6: Chemistry and Differentiation 2 92
6.1 Week 6 Tutorial Questions 92
6.2 Week 6 Tutorial Solutions 95

7 Week 7: Chemistry and Integration 1 106
7.1 Week 7 Tutorial Questions 106
7.2 Week 7 Tutorial Solutions 109



8 Week 8: Chemistry and Integration 2 113
8.1 Week 8 Tutorial Questions 113
8.2 Week 8 Tutorial Solutions 116

9 References 121

10 List of Formulae 122

Acknowledgements

I was pleased to respond to bookboon.com to write a textbook (which is split into 3 more manageable books, *Introductory Maths for Chemists*, *Intermediate Maths for Chemists*, and *Advanced Maths for Chemists* which should be studied in sequence) that would help Chemistry students survive, and 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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1 Week 1: Chemistry and Algebra 1

1.1 Introduction

This is the revised edition of *Introductory Maths for Chemists* (Parker 2011). The three books; *Introductory Maths for Chemists, 2nd edition,* (Parker 2013), *Intermediate Maths for Chemists* (Parker 2012) and *Advanced Maths for Chemists* (Parker 2013) are tutorial workbooks intended for first year undergraduates taking a degree in Chemistry or a Chemistry-related 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 and also to their Chemistry teachers and lecturers. The text is published as three books in order to reduce file size and make handling on a laptop or tablet computer much easier. *Introductory Maths for Chemists* roughly covers the first 8 weeks of semester 1; *Intermediate Maths for Chemists* the remainder of semester 1 and the beginning of semester 2; and *Advanced Maths for Chemists* the rest of semester 2. They each have 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.

Introductory Maths for Chemists is organized on a weekly basis. Go through the questions and work out the solution yourself on paper then check your solution. I give a full solution to show you the method of solving the problem. To begin with the solution gives 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.

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

1.1.1 Why Do Chemists Have To Do Maths?

Maths is a convenient and fast shorthand language that summarizes the details of a particular topic of Chemistry, it is the language of Chemistry. Maths is also the underlying language of all the Sciences, Engineering, Economics and many other subjects. So we won't be able to become really fluent in Chemistry until we understand its "shorthand" language.

1.1.2 How The Workbook Is Structured

At the beginning of your university Chemistry degree you may find that many of the chemistry examples used in this workbook have *not yet* been covered in your Chemistry course. *Don't worry* we are trying to understand the Maths at the moment not the Chemistry, and 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.

1.1.3 Physical Quantities

We start with reviewing Chemistry and Maths, this is spread over Weeks 1 and 2 and covers the underlying skills that all Chemists should be good at and which needs some practice. Some of this material you might have covered before but stick in there as it is vital to the rest of your degree course.

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 science and engineering all the variables we use are *physical quantities*, such as mass, length, time, force, work, enthalpy, entropy and so on. These physical quantities usually have a conventional symbol agreed by usage of the international community of scientists. 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 quite sure what it means exactly, $E = mc^2$. 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 book will get you accustomed to using Maths in the real world of manipulating equations made up of physical quantities written in the accepted scientific way.

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

Physical quantities consist of two parts, a pure number and a unit, which are inseparable. An example would be $c = 2.998 \times 10^8\ \text{m s}^{-1}$ where c is the symbol for the velocity of light. In order to clearly distinguish the three parts of the above equation, the physical quantity (or its symbol) is written in *italics* and the 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 we refer to the person then their name has an initial capital (Newton or Kelvin) but the unit name is all lower case (newton or kelvin) and the symbol for the unit is initial capital of one or sometimes two letters (N or K). The use of initial capital for units has a few exception (for historical reasons) *e.g.* the second (s), the kilogram (kg) and centimetre (cm). When we substitute a physical quantity for its symbol into an equation we must substitute *both* the number *and* the units into the equation, they are inseparable, they go together like the two sides of a piece of paper.

1.1.4 Linear or Straight Line Graphs

Straight line graphs are important in science and are very common. Linear graphs are particularly useful as being strong evidence that the Maths really does model the Chemistry, they are much easier to use in this way than curved graphs. They also allow you to spot any "rogue" or outlying experimental data points. A linear equation is of the form.

$$y = m\,x + c$$

Where x and y are the variables, m is the gradient of the line (how quickly y increases, or decreases, as x is increased), and c is the intercept on the y-axis (the "offset" that y starts with when $x = 0$) as in Fig. 1.1 (the data points are not shown for clarity).

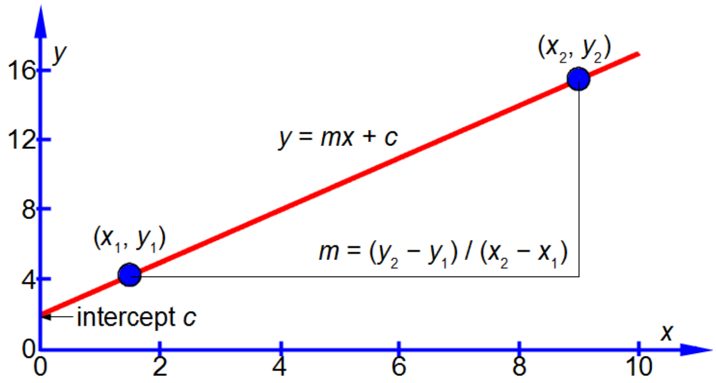


Figure 1.1: definition of the intercept and gradient for linear graph of $y = mx + c$.

The vertical axis is the y-axis and the horizontal axis is the x-axis. Whatever the names that are used for the variables in a particular situation, we should *always* say "plotting y against x" or "plotting y versus x" where the variable names are used instead of y and x. Once you have used your judgement to draw the best straight line (*e.g.* using a transparent ruler) then the equation of the best straight line is found as follows. Using the line itself *not* the data points, otherwise what was the point of drawing a best straight line, pick two positions on the line, one near the left hand side and one near the right hand side, shown in blue in Fig. 1.1. They are, respectively, (x_1, y_1) and (x_2, y_2) which I have measured from the full-sized hand-drawn graph to be (1.5, 4.25) and (9.0, 15.5). These two points give two simultaneous equations for $y = mx + c$.

$$\begin{aligned} (x_1, y_1) &= (1.5, 4.25) \qquad & 4.25 &= 1.5\,m + c \\ (x_2, y_2) &= (9.0, 15.5) \qquad & 15.5 &= 9.0\,m + c \end{aligned}$$

Subtracting the two simultaneous equations gives us the gradient m

$$11.25 = 7.5\ m \qquad m = 1.5$$

and adding the two simultaneous equations and using our value for m from above, we have

$$19.75 = 1.5 \times 10.5 + 2c \qquad c = 2.0$$

The equation for our straight line is thus

$$\boxed{y = 1.5\,x + 2.0}$$

In exams you will need to be able to *manually* plot a graph on graph paper and find the equation of the line. Computers, phones, and graphic calculators are *not* allowed, so practice with some of the tutorial questions!

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

In Chemistry often the equation that models the chemical behaviour is not a straight line function and then Maths is necessary to rearrange the equation to obtain a linear function that can be plotted as partial evidence that the original model actually agreed with the experimental data. Fig. 1.2 has a typical plot of data from a rearranged Arrhenius equation (which we discuss later). Firstly, notice how the axes are labelled as pure numbers.

Note that we plot the physical quantity divided by the unit
It is always a *pure number* that is plotted

Table *headings* just like axes of graphs and the table entries should always be written as
physical quantity divided by unit
The table headings and entries consists only of *pure numbers*

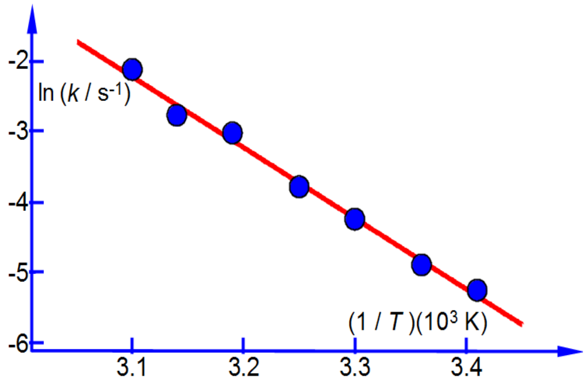


Figure 1.2: ln(k/s^{-1}) versus (1/T)(10^3 K).

Secondly, note the scales and the intersection of the axes.

> The graph axes should be scaled so that the data points fill most of the available space, this may require the axes of the graph to be moved so they don't intersect at (0, 0).
>
> As the origin (0, 0) is now a *long distance* away from your plotted data points, you should *not* try to find the intercept of such a graph by extrapolation, but *only* by finding the equation of the line you draw.

Thirdly, and perhaps a little confusing at first sight, is the fact that the x-axis in Fig. 1.2 is the reciprocal of temperature ($1/T$) and it is multiplied and not divided by a numerical factor. A lot of people have problems with this type of reciprocal labelling of axes, so I am going to spent some time going through it step by step. Let us take the temperature $T = 300$ K as an example for our x-axis labelling.

$$T = 300\ \mathrm{K} \qquad \frac{1}{T} = \frac{1}{300\ \mathrm{K}} \qquad \frac{1}{T} = 0.003333\ \mathrm{K}^{-1}$$

$$\frac{1}{T} = 3.333 \times \left(10^{-3}\ \mathrm{K}^{-1}\right) \qquad \frac{1}{T} \div \left(10^{-3}\ \mathrm{K}^{-1}\right) = 3.333$$

The x-axis could be labelled as in above-right, however, it is more clearly understood and more easily used in later processing of results when written in the following way

$$\left(\frac{1}{T}\right)\left(10^{3}\ \mathrm{K}\right) = 3.333$$

The y-axis label is easier to understand, we take the natural log of the pure number (k/s^{-1}) to give $\ln(k/\mathrm{s}^{-1})$ which is also a pure number. For Fig. 1.2 the best manual straight line ($y = mx + c$) is $y = -9.98x + 28.7$.

$$m = \frac{\Delta y}{\Delta x} = \frac{\ln\left(k/\mathrm{s}^{-1}\right)}{\left(\frac{1}{T}\right)\left(10^{3}\ \mathrm{K}\right)} = -9.98 \qquad m = \frac{\ln\left(k/\mathrm{s}^{-1}\right)}{\left(\frac{1}{T}\right)} = -9.98 \times 10^{3}\ \mathrm{K}$$

For the Arrhenius equation we will discover that the gradient equals $-E_{\mathrm{a}}/R$ where R is the gas constant and E_{a} is the activation energy. So from the gradient we can obtain the activation energy E_{a}.

$$m = -\frac{E_{\mathrm{a}}}{R} = -9.98 \times 10^{3}\ \mathrm{K} \qquad E_{\mathrm{a}} = -\left(-9.98 \times 10^{3}\ \mathrm{K}\right)\left(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)$$

$$E_{\mathrm{a}} = 82.97 \times 10^{3}\ \mathrm{J\ mol^{-1}} = 82.97\ \mathrm{kJ\ mol^{-1}}$$

From the equation of the best straight line for Fig. 1.2, the intercept $c = 28.7$ and because the intercept is defined as where the line meets the y-axis thus the intercept has the *same* units as the y-axis. From the Arrhenius equation the intercept is equal to $c = \ln(A)$. Don't worry too much if at the moment you are unsure of logs and antilogs as we will cover all of that area in Week 3 of this book.

$$c = \ln\left(A/\mathrm{s}^{-1}\right) = 28.7 \qquad A/\mathrm{s}^{-1} = 2.91 \times 10^{12} \qquad A = 2.91 \times 10^{12}\ \mathrm{s}^{-1}$$

Thus equation of the line in Fig. 1.2 is

$$\begin{array}{ccccccc} y & = & m & x & + & c \\ \ln\left(k/\mathrm{s}^{-1}\right) & = & \left(-9.98\times10^{3}\ \mathrm{K}\right) & \dfrac{1}{T} & + & \ln\left(2.91\times10^{12}\right) \end{array}$$

1.1.5 Suggested Textbooks

Introductory Maths for Chemists may be used with any Maths textbook, however, the students and I found the textbook (Stroud and Booth 2007) very useful. Despite its name of *Engineering Mathematics* Stroud and Booth's book covers *all* the Maths needed by all the sciences and engineering subjects. *Introductory Maths for Chemists* gives chemical examples of the Maths concepts. If you want to look up any first year chemistry then any General Chemistry textbook is useful but the textbook (Blackman, Bottle, Schmid, Mocerino and Wille 2012) is excellent. For later on in your course then both (Atkins and de Paula 2009) and (Levine 2009) have many examples of the interplay between Chemistry and Maths mainly in Physical Chemistry.

1.2 Week 1 Tutorial Questions

Remember you should work out your own solution on paper then check your solution and the method used. The solutions detailed here are only one way of achieving the result, don't worry if you arrive at the answer by a slightly different route as long as you are consistent and the answer is the same.

1.2.1 Question 1: Electromagnetic Radiation and Molecular Spectroscopy

Chemists use spectroscopic analysis all the time in the lab to determine what molecules are present in a sample and what are their concentrations. Spectroscopy is also used as a tool to understand the structure and reactions of molecules. Light, or electromagnetic radiation, consists of a moving wave of electric and magnetic fields which are at right angles to one another and also at right angles to the direction of travel, see Fig. 1.3 which for clarity only shows the electric field. In order to be able to use spectroscopy in chemistry we must understand light along with the Maths equations which summarize the properties of light.

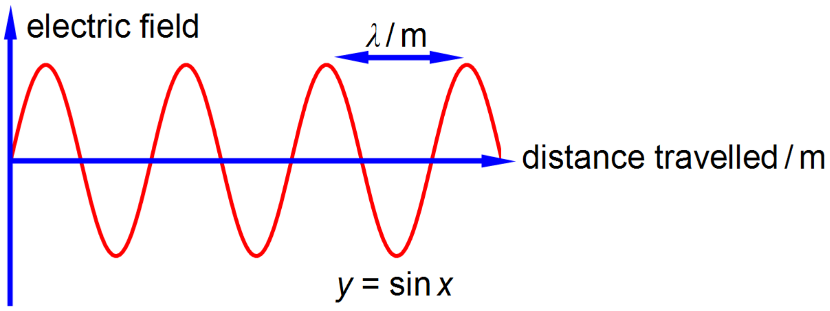


Figure 1.3: the oscillating electric field of light.

The wavelength λ (Greek letter “lambda”) is the distance between equivalent points on neighbouring waves. The correct symbol for frequency is ν (Greek letter “nu”) and it is the number of complete waves which pass a fixed point in a second, the units are “per second” or s^{-1} (sometimes called hertz). The velocity of light $c = 2.998\times10^{8}$ m s^{-1} is related to its wavelength and its frequency by

$$c = \lambda\,\nu$$

If a molecule absorbs light at a frequency of $\nu = 2.78\times10^{14}\ s^{-1}$ determine the wavelength λ of the light.

Jump to Solution 1 (see page 20)

1.2.2 Question 2: The Concentration of Molecules in Solutions

Chemists routinely need to know and alter the concentrations of solutions in the lab. The concentration of a solute is c mol L^{-1} and is given in terms of the number of moles of the solute, n mol, and the volume of the solution, V, measured in litres, symbol L. The SI unit of volume is the metre cubed m^3 which is 1000 L, however, chemists often use the sub-multiple unit litre as it is more convenient than the cubic metre. The litre, L, is identical to the decimetre cubed, dm^3.

$$c = \frac{n}{V}$$

If 5 mL of a 0.1 mol L^{-1} aqueous solution is diluted with 10 mL of water, calculate the concentration of the new solution. Note that mL is the correct symbol for millilitre or one thousandth of a litre L (rather than the old-fashioned symbol ml which is still commonly seen).

Jump to Solution 2 (see page 21)

1.2.3 Question 3: Chemical Equilibrium

Some chemical reactions may have come to an equilibrium,

$$\mathrm{A} + 2\mathrm{B} \rightleftharpoons 3\mathrm{C} + 2\mathrm{D}$$

At a given temperature this reaction will eventually come to equilibrium, the double half-arrows indicate that both the forward reaction and the reverse reaction are still occurring simultaneously and the rates of the forward and reverse reactions have become equal at equilibrium. Once the reaction has reached equilibrium the concentrations of the reactants and products are then constant and are related to one another by the reaction's equilibrium constant K_c which is characteristic of the reaction at that temperature. For solutions, the concentrations (*e.g.* c_{A}) are conventionally written as a pure number, with the molecule's symbol in square brackets, *e.g.* [A], times the units of mol L^{-1}.

$$c_{\mathrm{A}} = [\mathrm{A}]\,\mathrm{mol\ L^{-1}} \qquad c_{\mathrm{B}} = [\mathrm{B}]\,\mathrm{mol\ L^{-1}} \qquad c_{\mathrm{C}} = [\mathrm{C}]\,\mathrm{mol\ L^{-1}} \qquad c_{\mathrm{D}} = [\mathrm{D}]\,\mathrm{mol\ L^{-1}}$$

$$K_{\mathrm{c}} = \frac{\left(\dfrac{c_{\mathrm{C}}}{c^{\mathrm{o}}_{\mathrm{C}}}\right)^{3}\left(\dfrac{c_{\mathrm{D}}}{c^{\mathrm{o}}_{\mathrm{D}}}\right)^{2}}{\left(\dfrac{c_{\mathrm{A}}}{c^{\mathrm{o}}_{\mathrm{A}}}\right)\left(\dfrac{c_{\mathrm{B}}}{c^{\mathrm{o}}_{\mathrm{B}}}\right)^{2}} \qquad K_{\mathrm{c}} = \frac{\left(\dfrac{[\mathrm{C}]\,\mathrm{mol\ L^{-1}}}{1\ \mathrm{mol\ L^{-1}}}\right)^{3}\left(\dfrac{[\mathrm{D}]\,\mathrm{mol\ L^{-1}}}{1\ \mathrm{mol\ L^{-1}}}\right)^{2}}{\left(\dfrac{[\mathrm{A}]\,\mathrm{mol\ L^{-1}}}{1\ \mathrm{mol\ L^{-1}}}\right)\left(\dfrac{[\mathrm{B}]\,\mathrm{mol\ L^{-1}}}{1\ \mathrm{mol\ L^{-1}}}\right)^{2}}$$

In the equation for K_c each concentration is divided by its own standard state concentration. We use as the symbol for standard state a superscript degree which is pronounced as "naught", "zero" or "standard". For solutes, the standard state concentration are *e.g.* $c^{\mathrm{o}}{}_{\mathrm{A}} = 1$ mol L^{-1}. The units will cancel out to give the pure number "dimensionless concentrations" *e.g.* [A]. So Kc the equilibrium constant must also be dimensionless. In chemical equilibria each of the concentrations is raised to the same power as its stoichiometric coefficient.

$$K_{\mathrm{c}} = \frac{[\mathrm{C}]^{3}[\mathrm{D}]^{2}}{[\mathrm{A}][\mathrm{B}]^{2}}$$

Firstly, for the above equilibrium reaction calculate the value of the equilibrium constant K_c in a solution where all four of the concentrations are equal to 0.1 mol L^{-1}. Secondly, calculate the new concentration of [C] if we alter the concentrations to $[A] = 0.2 \text{ mol L}^{-1}$, $[B] = 0.15 \text{ mol L}^{-1}$ and $[D] = 0.25 \text{ mol L}^{-1}$?

Jump to Solution 3 (see page 22)

1.2.4 Question 4: Heats of Reaction and Temperature

The enthalpy change for a chemical reaction is ΔH_1 at temperature T_1 and ΔH_2 at temperature T_2. In science we always show a change in a variable as *final* minus *original*. So the change in temperature is $T_2 - T_1$ which leads to a change in the reaction enthalpy of $\Delta H_2 - \Delta H_1$.

$$\Delta H_2 - \Delta H_1 = C_p\left(T_2 - T_1\right)$$

The constant C_p shows how sensitive the reaction enthalpy is to a change in temperature and C_p is called the heat capacity at constant pressure. Rearrange the above equation to get T_1 as the subject of the equation.

Jump to Solution 4 (see page 23)

1.2.5 Question 5: Kinetics of a Complex Chemical Reaction

The reaction at high temperature between H_2 and Br_2 molecules in the gas phase gives HBr molecules.

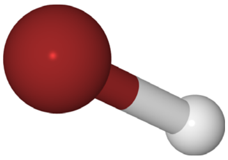


Figure 1.4: HBr, H = grey, Br = red.

Studying the chemical kinetics of this reaction, chemists have found that the rate of formation of HBr molecules v is as given below where k and k' are parameters which only depend upon the temperature of the reaction. The symbol v for rate of reaction ("vee" as in velocity) should *not* be confused with the Greek letter v ("nu") with the context removing any confusion. The concentration of *e.g.* H_2 is $[H_2]$ mol L^{-1} but for clarity reaction rate equations are usually written without the units being explicitly shown.

$$v = \frac{k\left[\mathrm{H_2}\right]\left[\mathrm{Br_2}\right]^{3/2}}{\left[\mathrm{Br_2}\right] + k'\left[\mathrm{HBr}\right]}$$

Firstly, rearrange this equation for plotting as a straight line graph of $1/v$ against [HBr] by first taking reciprocals of both sides. Then simplify the right hand side of the new equation to get the final form which is ready for a linear plot. Second, what are the gradients and intercepts of this equation?

Jump to Solution 5 (see page 23)

1.2.6 Question 6: Non-Ideal Gases

The van der Waals equation below, models the behaviour of many non-ideal gases over wide pressure and temperature ranges.

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

Where p is the pressure; V the volume; T the temperature; n the number of moles of gas; R is the gas constant R = 8.314 J K^{-1} mol^{-1}; and a and b are constants which have characteristic values for a given molecule. The constant a reflects the attractive London dispersion forces between the molecules, this reduces the pressure exerted on the container walls. The constant b reflects the "excluded volume" of a molecule. All molecules have a certain radius and other molecules cannot occupy the same space, this excluded volume has the effect of reducing the available volume for the movement of the molecules. Rearrange the van der Waals equation to obtain the pressure as the subject of the equation.

Jump to Solution 6 (see page 25)

1.2.7 Question 7: Vapour Pressure of Liquids

The gas phase pressure of a liquid is called its vapour pressure p and increases with increasing temperature of the liquid

$$\ln\left(\frac{p_2}{p_1}\right)=\frac{\Delta H^{o}_{\text{vap}}}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

Where $\Delta H^{o}_{\text{vap}}$ is the enthalpy of vaporization, the amount of heat required to vaporize a mole of liquid in its standard state; R is the gas constant; and T_1 and T_2 are low and high temperatures having p_1 and p_2 vapour pressures. Rearrange the equation to get T_2 as the subject of the equation.

Jump to Solution 7 (see page 25)

1.2.8 Question 8: Kinetics of a Second-Order Chemical Reaction

An example of a second-order reaction is the atmospheric reaction between nitric oxide (NO) and chlorine (Cl_2). The superscript dots indicate radicals *i.e.* unpaired electrons. Nitrosyl chloride NOCl is a yellow gas first described in 1831.

$$\text{NO}^{\bullet}+\text{Cl}_2 \longrightarrow \text{NOCl}+\text{Cl}^{\bullet}$$

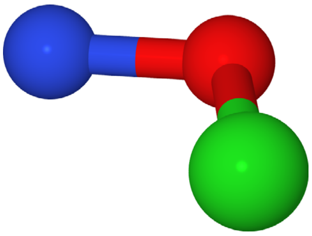


Figure 1.5: nitrosyl chloride N = blue, O = red, Cl = green.

The speed of a second-order chemical reaction

$$\text{A}+\text{B}\longrightarrow \text{product}$$

depends on the concentrations of both the molecules A and B. The rate of reaction is summarized by an equation which includes the following term as part of the equation. Where a_0 and b_0 are the initial concentrations of molecules A and B and x is the *change* in concentration of both the reactants. Simplify this expression using partial fractions.

$$\frac{1}{(a_0-x)(b_0-x)}$$

Jump to Solution 8 (see page 26)

1.2.9 Question 9: Isotope Abundances of Molecules

The binomial formula

$$\binom{n}{k} = \frac{n!}{k!\,(n-k)!}$$

is used in chemistry for: (a) calculating the intensities of NMR (nuclear magnetic resonance) lines due to spin-spin splitting (Pascal's triangle); (b) in mass spectrometry for calculating the ion abundances (intensities) for elements with several isotopes; (c) to model the biochemical transition between the helix and coiled structures of proteins; and (d) in statistical mechanics to calculate the probabilities of a given distribution of molecules over a set of quantum states. You will meet all of these techniques later on in your Chemistry degree.

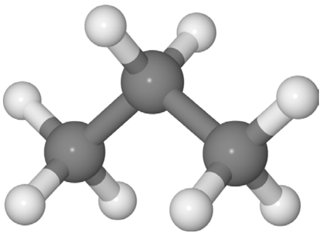


Figure 1.6: propane H = grey, C = dark grey.

The natural abundance of the stable carbon isotopes are $^{13}C \approx 1\%$ and $^{12}C \approx 99\%$. Calculate the isotopic abundances arising from just the three carbon atoms in propane (ignoring the H-atom isotopes) by expanding the binomial formula $(1 + 99)^3$ into the first 4 terms. These 4 terms correspond to the relative amounts of the following four isotopic molecules $^{13}C_3H_8$, $^{13}C_2{}^{12}CH_8$, $^{13}C^{12}C_2H_8$, and $^{12}C_3H_8$ (these isotopic variants are called isotopomers).

Jump to Solution 9 (see page 27)

1.3 Week 1 Tutorial Solutions

1.3.1 Solution 1: Electromagnetic Radiation and Molecular Spectroscopy

Rearranging the equation so that the unknown quantity λ is the subject of the equation is most clearly done by dividing both sides of the equation by the frequency ν.

$$c = \lambda\nu \qquad \frac{c}{\nu} = \frac{\lambda\nu}{\nu}$$

Cancelling top and bottom within any single term, then rearranging the equation to make λ the subject,

$$\frac{c}{\nu} = \frac{\lambda\cancel{\nu}}{\cancel{\nu}} \qquad \frac{c}{\nu} = \lambda \qquad \lambda = \frac{c}{\nu}$$

We say that λ is the subject of the equation when it is on the left of the equal sign and is equal to the rest of the equation. To make this physically meaningful we must substitute the physical quantities, numbers and units, for the symbols and then cancel the units within any single term. In this case it is s^{-1} that cancels to give the wavelength with the units *determined* by the correct use of physical quantities.

$$\lambda = \frac{c}{\nu} \qquad \lambda = \frac{2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}}}{2.78 \times 10^{14}\ \cancel{\text{s}^{-1}}}$$

$$\lambda = 1.0784 \times 10^{-6}\ \text{m}$$

Return to Question 1 (see page 14)

1.3.2 Solution 2: The Concentration of Molecules in Solutions

The number of moles of the solute remains constant when the concentration is altered by diluting the solution with more solvent, n is constant as c varies. Rearranging the equation so that the unknown constant quantity n becomes the subject of the equation and then substituting in the *original* physical quantities,

$$c = \frac{n}{V} \qquad n = c\,V \qquad n = \left(0.1\ \text{mol L}^{-1}\right)\left(0.005\ \text{L}\right)$$

$$n = 5 \times 10^{-4}\ \text{mol}$$

It is usually less confusing to carry out calculations in the base unit, here the L, rather than multiples or sub-multiples such as the mL.

Return to Question 2 (see page 15)

1.3.3 Solution 3: Chemical Equilibrium

Firstly, we need to find the value for the equilibrium constant,

$$K_c = \frac{[C]^3[D]^2}{[A][B]^2} \qquad K_c = \frac{[0.1]^3[0.1]^2}{[0.1][0.1]^2}$$

$$K_c = 0.01$$

Secondly, we rearrange the equilibrium constant equation so that [C] is the subject of the equation. This is done sequentially by: (1) multiplying both sides of the equation by $[A][B]^2$; (2) and then cancelling out top and bottom within any single term;

$$K_c = \frac{[C]^3[D]^2}{[A][B]^2} \qquad K_c[A][B]^2 = \frac{[C]^3[D]^2}{\cancel{[A]}\cancel{[B]^2}}\cancel{[A]}\cancel{[B]^2} \qquad K_c[A][B]^2 = [C]^3[D]^2$$

(3) then dividing by $[D]^2$ on both sides of the equation and cancelling top and bottom within any single term;

$$\frac{K_c[A][B]^2}{[D]^2} = \frac{[C]^3\cancel{[D]^2}}{\cancel{[D]^2}} = [C]^3$$

(4) writing $[C]^3$ as the subject; (5) substituting in the physical quantities; and (6) taking the cube root of $[C]^3$ gives the concentration of molecule C.

$$[C]^3 = \frac{K_c[A][B]^2}{[D]^2} = \frac{0.01 \times 0.2 \times (0.15)^2}{(0.25)^2} = 7.2 \times 10^{-4}$$

As [C] is the symbol for the pure number of the concentration, so the concentration in mol L^{-1} is

$$[C] = 8.96 \times 10^{-2} \qquad c_C = [C]\,\text{mol L}^{-1} \qquad c_C = 8.96 \times 10^{-2}\,\text{mol L}^{-1}$$

Increasing the concentrations of [A], [B] and [D] has decreased the concentrations of [C] in order to maintain the equilibrium constant K_c at a constant value.

Return to Question 3 (see page 16)

1.3.4 Solution 4: Heats of Reaction and Temperature

The lower temperature T_1 is inside the bracket and so we need to multiply out the bracket, rearrange the equation to get C_pT_1 as the subject and finally divide throughout by C_p.

$$\Delta H_2 - \Delta H_1 = C_pT_2 - C_pT_1 \qquad C_pT_1 = C_pT_2 - \Delta H_2 + \Delta H_1 \qquad T_1 = T_2 - \frac{\Delta H_2}{C_p} + \frac{\Delta H_1}{C_p}$$

This is perfectly correct but you may also have taken it one step further to the alternative, neater form.

$$T_1 = T_2 - \frac{\Delta H_2 - \Delta H_1}{C_p}$$

Return to Question 4 (see page 17)

1.3.5 Solution 5: Kinetics of a Complex Chemical Reaction

$$v = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}{[\mathrm{Br_2}] + k'[\mathrm{HBr}]} \qquad \frac{1}{v} = \frac{[\mathrm{Br_2}] + k'[\mathrm{HBr}]}{k[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}} \qquad \frac{1}{v} = \frac{[\mathrm{Br_2}]}{k[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}} + \frac{k'[\mathrm{HBr}]}{k[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}$$

We have taken reciprocals on both sides of the equation and then the right hand term can be split into two terms with the same denominator. The first of these two terms may then be simplified further by cancelling out $[\mathrm{Br_2}]$ top and bottom to give a straight line graph ($y = c + mx$) of $1/v$ against [HBr] as in Fig 1.7.

$$\frac{1}{v} = \frac{1}{k[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}} + \frac{k'[\mathrm{HBr}]}{k[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}$$

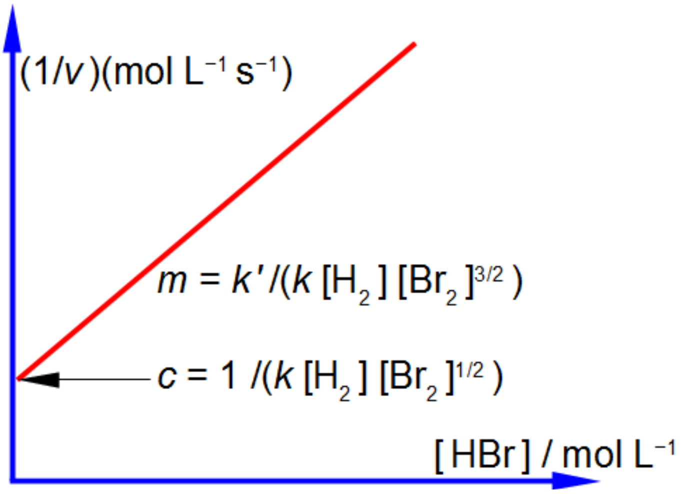


Figure 1.7: linear graph for H_2/Br_2 reaction.

Return to Question 5 (see page 17)

1.3.6 Solution 6: Non-Ideal Gases

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

Sequentially: (1) divide both sides by (V – nb); (2) cancel out within any single term; (3) subtract (n^2a/V^2) from both sides; (4) and you may want to put the square terms inside a bracket to tidy up the rearranged equation.

$$p+\frac{n^2 a}{V^2}=\frac{nRT}{V-nb} \qquad p=\frac{nRT}{V-nb}-\frac{n^2 a}{V^2}$$

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

Return to Question 6 (see page 18)

1.3 7 Solution 7: Vapour Pressure of Liquids

This question is not as easy as it first appears. The method suggested is one of several but with this type of question it is easy to make a mistake and obtain an incorrect solution, a step by step method is best.

$$\ln\left(\frac{p_2}{p_1}\right)=\frac{\Delta H^{o}_{\text{vap}}}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

(1) split the term in brackets into two terms; (2) cancel out top and bottom separately for each term inside the right hand bracket; (3) expand the bracket by multiplying it out;

$$\ln\left(\frac{p_2}{p_1}\right)=\frac{\Delta H^{o}_{\text{vap}}}{R}\left(\frac{\cancel{T_2}}{T_1\cancel{T_2}}-\frac{\cancel{T_1}}{\cancel{T_1}T_2}\right)$$

$$\ln\left(\frac{p_2}{p_1}\right)=\frac{\Delta H^{o}_{\text{vap}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad \ln\left(\frac{p_2}{p_1}\right)=\frac{\Delta H^{o}_{\text{vap}}}{RT_1}-\frac{\Delta H^{o}_{\text{vap}}}{RT_2}$$

then (4) rearrange the equation so that the term containing T_2 becomes the subject; (5) multiply by $R/\Delta H^{o}_{\text{vap}}$ throughout and (6) then cancelling out top and bottom within each term;

$$\frac{\Delta H^{o}_{\text{vap}}}{RT_2}=\frac{\Delta H^{o}_{\text{vap}}}{RT_1}-\ln\left(\frac{p_2}{p_1}\right) \qquad \frac{1}{T_2}=\frac{1}{T_1}-\frac{R\ln(p_2/p_1)}{\Delta H^{o}_{\text{vap}}}$$

(7) before we can take the reciprocal on both sides we need to bring the right hand side to the common denominator $T_1 \Delta H^{o}_{\text{vap}}$ and finally (8) we can now take reciprocals on both sides of the equation.

$$\frac{1}{T_2} = \frac{\Delta H^{o}_{\text{vap}} - R T_1 \ln\left(p_2/p_1\right)}{T_1 \Delta H^{o}_{\text{vap}}}$$

$$T_2 = \frac{T_1 \Delta H^{o}_{\text{vap}}}{\Delta H^{o}_{\text{vap}} - R T_1 \ln\left(p_2/p_1\right)}$$

Return to Question 7 (see page 19)

1.3.8 Solution 8: Kinetics of a Second-Order Chemical Reaction

In order to simplify the expression using partial fractions we use two undefined coefficients, A and B, whose values we shall determine later on. In the partial fraction, note that the sign ≡ means "identical to" and that an *identity* is true for *all* values of x. For an *equation*, however, the left hand side is *only* equal to the right hand side for *certain* values of x which are called the solutions or roots of the equation.

$$\frac{1}{\left(a_0 - x\right)\left(b_0 - x\right)} \equiv \frac{A}{\left(a_0 - x\right)} + \frac{B}{\left(b_0 - x\right)}$$

Multiply left and right of the identity by $(a_o - x)(b_o - x)$ and cancel out where possible in any single term.

$$\frac{\left(a_0 - x\right)\left(b_0 - x\right)}{\left(a_0 - x\right)\left(b_0 - x\right)} \equiv \frac{A\left(a_0 - x\right)\left(b_0 - x\right)}{\left(a_0 - x\right)} + \frac{B\left(a_0 - x\right)\left(b_0 - x\right)}{\left(b_0 - x\right)} \qquad 1 \equiv A\left(b_0 - x\right) + B\left(a_0 - x\right)$$

This identity is true for *all* values of x. Firstly, to find the unknown constant B we set $x = b_0$.

$$1 \equiv A\left(b_0 - x\right) + B\left(a_0 - x\right) \qquad 1 \equiv \left(A \times 0\right) + B\left(a_0 - b_0\right) \qquad B \equiv \frac{1}{\left(a_0 - b_0\right)}$$

Secondly, to find the unknown constant A we set $x = a_0$.

$$1 \equiv A\left(b_0 - x\right) + B\left(a_0 - x\right) \qquad 1 \equiv A\left(b_0 - a_0\right) + \left(B \times 0\right) \qquad A \equiv \frac{1}{\left(b_0 - a_0\right)}$$

Note that $A = -B$ or

$$A \equiv \frac{1}{\left(b_0 - a_0\right)} \qquad B \equiv -\frac{1}{\left(b_0 - a_0\right)}$$

Substituting these later values for A and B into our original identity for partial fractions (in yellow) gives,

$$\frac{1}{(a_0-x)(b_0-x)} \equiv \frac{A}{(a_0-x)} + \frac{B}{(b_0-x)} \equiv \frac{1}{(b_0-a_0)(a_0-x)} - \frac{1}{(b_0-a_0)(b_0-x)}$$

Notice the minus sign, we can introduce brackets to clean things up on the right hand side.

$$\frac{1}{(a_0-x)(b_0-x)} \equiv \frac{1}{b_0-a_0}\left(\frac{1}{a_0-x} - \frac{1}{b_0-x}\right)$$

Return to Question 8 (see page 19)

1.3.9 Solution 9: Isotope Abundances of Molecules

$$\binom{n}{k}$$

The shorthand notation used above is called the "binomial bracket". There is no dividing line and it does *not* mean n divided by k. It is pronounced "n choose k" and by the binomial theorem it is equal to

$$\binom{n}{k} = \frac{n!}{k!\,(n-k)!}$$

Where a factorial is defined as

$$n! = n(n-1)(n-2)(n-3)\cdots 1 \quad \text{and by definition} \quad 0! = 1$$

The carbon atom isotopic abundances in propane are found by expanding the binomial bracket below for the four different isotopomers which "choose" 0, 1, 2, or 3 carbons out of three carbons to be ^{12}C.

$$(1+99)^3 = 1 + \binom{3}{1}99 + \binom{3}{2}99^2 + \binom{3}{3}99^3$$

Expanding the binomial formulae gives

$$(1+99)^3 = 1 + \frac{3!}{1!\,2!}99 + \frac{3!}{2!\,1!}99^2 + \frac{3!}{3!\,0!}99^3$$

$$(1+99)^3 = 1 + \frac{3\times2\times1}{1\times2\times1}99 + \frac{3\times2\times1}{2\times1\times1}99^2 + \frac{3\times2\times1}{3\times2\times1\times1}99^3$$

Cancelling out terms top and bottom within any single term, gives

$$(1+99)^3 = 1 + (3\times99) + (3\times99^2) + (1\times99^3) = 1 + (297) + (29403) + (970299)$$

In mass spectrometry we normally express the ratios as a percentage of the largest abundance to give the following predicted mass spectrum. Notice how rarely we would find in our mass spectrometer a propane molecule with *three* ^{13}C atoms (about one in a million propane molecules). On the other hand, just over 3% of the propane molecules contain *one* ^{13}C atom.

$^{13}C_3H_8$	$^{13}C_2\,^{12}CH_8$	$^{13}C\,^{12}C_2H_8$	$^{12}C_3H_8$
1	297	29403	970299
0.00010%	0.031%	3.03%	100%

Return to Question 9 (see page 20)

2 Week 2: Chemistry and Algebra 2

2.1 Week 2 Tutorial Questions

2.1.1 Question 1: Energy of a Single Photon

Chemical spectroscopy and analytical chemistry use light of various types not just visible light but also other regions of the electromagnetic spectrum. The quantum mechanics view of light is that when it is treated as a particle it is made up of a stream of photons. The energy of a single photon, E, is the product of Planck's constant $h = 6.626\times10^{-34}$ J s and the frequency of the light ν ("nu"). So this equation combines the particle view of light on the left hand side (the energy of a photon) with the wave view of light on the right hand side of the equation (the frequency of a wave), *i.e.* this equation embodies wave-particle duality!

$$E = h\nu$$

As mentioned in section 1.2.1 when light is treated as a wave we have an equation that relates the frequency ν and the wavelength λ of light to the velocity of light c.

$$c = \lambda\nu$$

Where $c = 2.998\times10^{8}\ \mathrm{m\ s^{-1}}$ is the speed of light. Combine these two equations and calculate the energy of a single photon of wavelength λ = 427 nm (the symbol nm stands for a unit called a nanometre or 10^{-9} m).

Jump to Solution 1 (see page 41)

2.1.2 Question 2: Rates of Chemical Reactions and Concentrations

$$\mathrm{A + B \longrightarrow C}$$

A particular chemical reaction has a rate or speed v ("vee" as in velocity) given in terms of the concentrations of the reactants and products (indicted by square brackets) and the rate constant k. For *clarity* we have not included the units in the rate equation, this is the normal convention in kinetic rate equations purely for clarity. This particular reaction's rate is experimentally found to depend upon the square of the concentration of the reactant A, the cube of the concentration of the reactant B and is inversely proportional to the concentration of the product C.

$$v_{\mathrm{initial}} = k\frac{[\mathrm{A}]^2[\mathrm{B}]^3}{[\mathrm{C}]}$$

Calculate the rate of reaction if the concentrations of A, B, C are all doubled by finding the ratio of the final rate of reaction, v_{final},, to the initial rate of reaction v_{intial}..

Jump to Solution 2 (see page 41)

2.1.3 Question 3: The Strength of an Ionic Crystal Structure

An ionic crystal MX with M being the metal cation and X the non-metal anion (*e.g.* Fig. 2.1) has a certain amount of intrinsic strength that holds the crystal structure together. This is called the lattice enthalpy $\Delta H^{o}_{\text{lattice}}$ and is given by the equation,

$$\Delta H^{o}_{\text{lattice}} = -\Delta H^{o}_{\text{formation}} + \Delta H^{o}_{\text{sublimation}} + \frac{1}{2}\Delta H^{o}_{\text{dissociation}} + \Delta H^{o}_{\text{ionization}} + \Delta H^{o}_{\text{electron gain}}$$

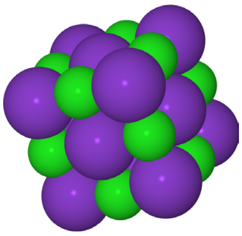
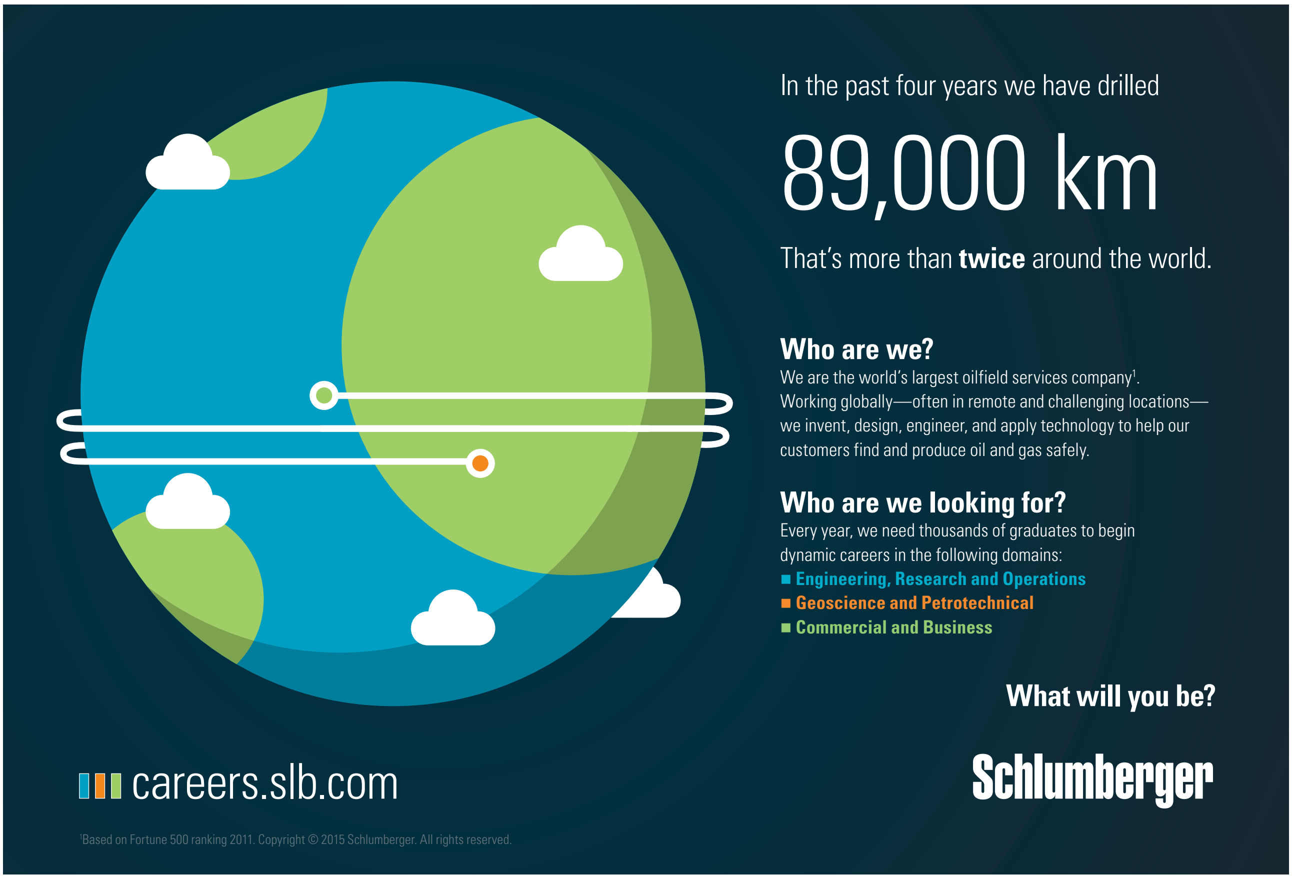


Figure 2.1: a small section of a KCl crystal, K^+ = purple, Cl^- = green.



The other physical quantities in the equation are for the present not important, although you will come across them early on in your Chemistry degree. Given the following data for potassium chloride crystals rearrange the above equation and calculate the enthalpy of electron gain $\Delta H^{o}_{\text{electron gain}}$ for the Cl^{-} anion.

$-\Delta H^{o}_{\text{formation}}$	$\Delta H^{o}_{\text{sublimation}}$	$\Delta H^{o}_{\text{dissociation}}$	$\Delta H^{o}_{\text{ionization}}$	$\Delta H^{o}_{\text{electron gain}}$
$-437\ \text{kJ mol}^{-1}$	$+89\ \text{kJ mol}^{-1}$	$+244\ \text{kJ mol}^{-1}$	$+418\ \text{kJ mol}^{-1}$	$+717\ \text{kJ mol}^{-1}$

Jump to Solution 3 (see page 42)

2.1.4 Question 4: Kinetics of Isomerization

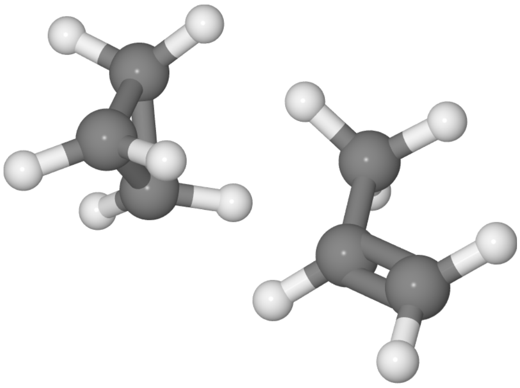


Figure 2.2: isomerization from cyclopropane to propene, H = grey, C = dark grey.

In the Lindemann chemical kinetic treatment of the isomerization of molecule A to its isomer B, as in the isomerization reaction of cyclopropane to propene, Fig. 2.2, we have

$$\text{A} \rightleftarrows \text{B}$$

The double full-arrows indicate that the reactions have not yet come to equilibrium. During the algebraic manipulation the following kinetic equation is obtained.

$$k_1[\text{A}]^2 - k_2[\text{A}^*][\text{A}] - k_3[\text{A}^*] = 0$$

where A* is a reaction *intermediate* which is chemically different from A and is roughly “half way” between the structures of A and B. The Lindemann mechanism of isomerization will be covered later on in your Chemistry lectures. The square brackets indicate concentrations of the different molecules A and A* involved and for clarity the units have not been shown. Rearrange the equation to get [A*]the concentration of the reaction intermediate as the subject.

Jump to Solution 4 (see page 43)

2.1.5 Question 5: Enthalpy of Combustion of Benzene

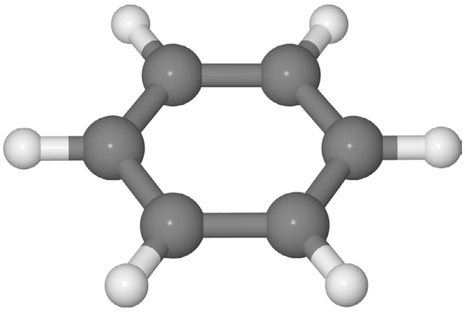


Figure 2.3: benzene, H = grey, C = dark grey.

When benzene, Fig. 2.3, is combusted it has the following stoichiometric reaction

$$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6\,CO_2 + 3\,H_2O$$

The enthalpy change for this combustion reaction is equal to the sum of the standard enthalpies of formation $\Delta H^o{}_f$ of the products minus the sum of the standard enthalpies of formation of the reactants. Each enthalpy of formation being multiplied by the stoichiometric coefficient for that molecule. Enthalpy of formation is covered during your first year of your degree.

$$\Delta H^o_{comb} = 6\,\Delta H^o_f(CO_2) + 3\,\Delta H^o_f(H_2O) - \left(\Delta H^o_f(C_6H_6) + \frac{15}{2}\Delta H^o_f(O_2)\right)$$

Rearrange the enthalpy equation to get the enthalpy of formation of benzene as the subject of the equation.

Jump to Solution 5 (see page 44)

2.1.6 Question 6: Hydrogen-Atom Spectroscopy

The Rydberg equation very accurately summarizes the UV-visible electronic spectroscopy that is observed for the hydrogen atom. It gives the wavenumber $\bar{\nu}$ (pronounced "nu bar") of the light emitted or absorbed by a H-atom in terms of jumps of the single electron between two quantized energy levels.

$$\bar{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Wavenumber (units of cm^{-1} pronounced as "centimetres to the minus one" or "reciprocal centimetres") is for the wave nature of light the number of complete light waves per centimetre as in Fig. 2.4.

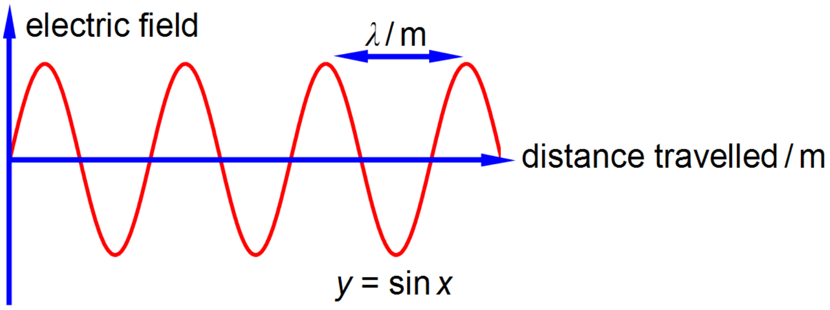


Figure 2.4: the electric field of a light wave.

The quantized energy levels are called atomic orbitals (AOs) and are characterized by the two principal quantum numbers n_1 for the initial AO and n_2 for the final AO involved in the jump. R_H is the Rydberg constant. Rearrange the equation to obtain n_2 as the subject of the equation.

Jump to Solution 6 (see page 44)

2.1.7 Question 7: Chemical Equilibrium and Concentration Calculations

$$H_2 + I_2 \rightleftharpoons 2\,HI$$

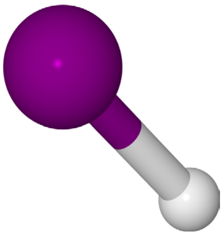


Figure 2.5: hydrogen iodide H = grey, I = purple.

The above chemical reaction when carried out at a temperature of 425°C has the I_2, HI and H_2 all in the gas phase. The chemical symbol of the two half-arrows indicates that the reaction is at a dynamic equilibrium going in both directions simultaneously. This reaction has an equilibrium constant K_c of 55.64 at 425°C.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 55.64$$

If we originally placed 2 mol L^{-1} of H_2 and 2 mol L^{-1} of I_2 in a flask at 425°C with no HI present, calculate the equilibrium concentrations of H_2, I_2 and HI when equilibrium is achieved at this temperature?The way we tackle this type of question is to assume that x moles of H_2 and I_2 are consumed in going from the above original conditions to equilibrium and $2x$ moles of HI are formed when equilibrium is achieved. The concentrations at equilibrium are then

$$\begin{array}{ccccc} H_2 & + & I_2 & \rightleftharpoons & 2\,HI \\ (2-x) & + & (2-x) & \rightleftharpoons & 2\,x \end{array}$$

$$K_c = \frac{[2\,x]^2}{[2-x][2-x]} = 55.64$$

The rather difficult Chemistry problem comes down to solving the Maths for x in this equation. Solve this equation in the most efficient manner which may not necessarily be by the use of the quadratic formula. Then using the chemically sensible value of x from your solution, work out the equilibrium concentrations for the three molecules.

Jump to Solution 7 (see page 46)

2.1.8 Question 8: Crystal Structures by X-Ray Diffraction

When a molecule forms a crystalline solid we can use X-ray diffraction to determine the positions of the atoms within the molecule. X-rays are very short wavelength light with wavelengths of roughly the diameter, or less, of an atom. The Bragg equation below gives the scattering angles θ where bright “reflections” of monochromatic X-rays are detected from layers of *equivalent* atoms within the crystal.

$$n\,\lambda = 2\,d\sin(\theta)$$

Where λ is the wavelength of the X-rays, d is the spacing between the lattice planes of equivalent atoms in the crystal, θ is the scattering angle and $n = 1, 2, 3,$ is the order of the reflection (quantum numbers such as n are dimensionless, they are pure numbers). Calculate the lattice spacing d when using radiation of wavelength $\lambda = 0.154$ nm for $n = 1$ at a scattering angle $\theta = 11°$. Specify the units for your calculated d value. The symbol nm stands for a nanometre or 10^{-9} m.

Jump to Solution 8 (see page 47)

2.1.9 Question 9: Polymer Chemistry

Long polymer molecules tend to coil up rather than being stretched out straight, Fig. 2.6 is an example of a *short* polythene molecule.

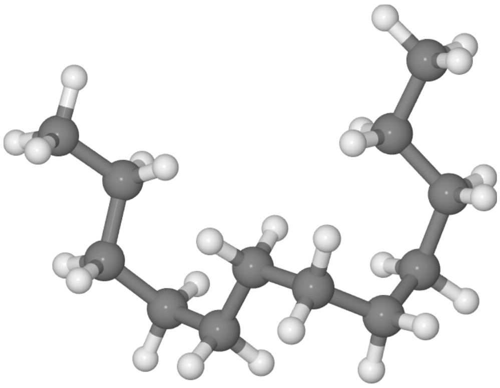


Figure 2.6: randomly coiled polyethylene, H = grey, C = dark grey.

Looking at a large number of such randomly coiled molecules, the average end-to-end distance r of the polymer molecules is given by

$$r^2 = N\,l^2\,\frac{1-\cos(\theta)}{1+\cos(\theta)}$$

Where the polymer consists of N chemical bonds making up the backbone of the polymer chain, with a monomer length of l, and θ the C-atom bond angle. Calculate the average end-to-end distance, r, for a polymer with $\theta = 109.5°$ (the tetrahedral angle), $l = 154$ pm and $N = 5\times10^3$. Specify the units for your calculated r value. The symbol pm stands for a picometre or 10^{-12} m which is a common multiple unit for the sizes of atoms and chemical bonds.

Jump to Solution 9 (see page 47)

2.1.10 Question 10: Conjugated Molecules and Quantum Chemistry

A conjugated molecule (also called a polyene) is one with alternating single and double carbon-carbon bonds in its backbone.

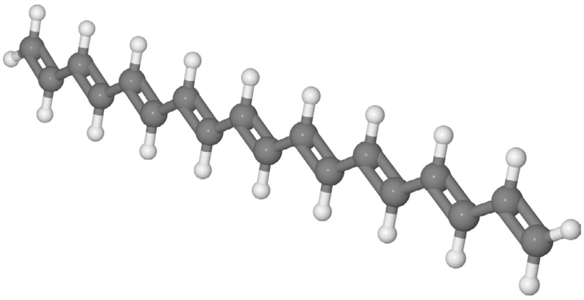
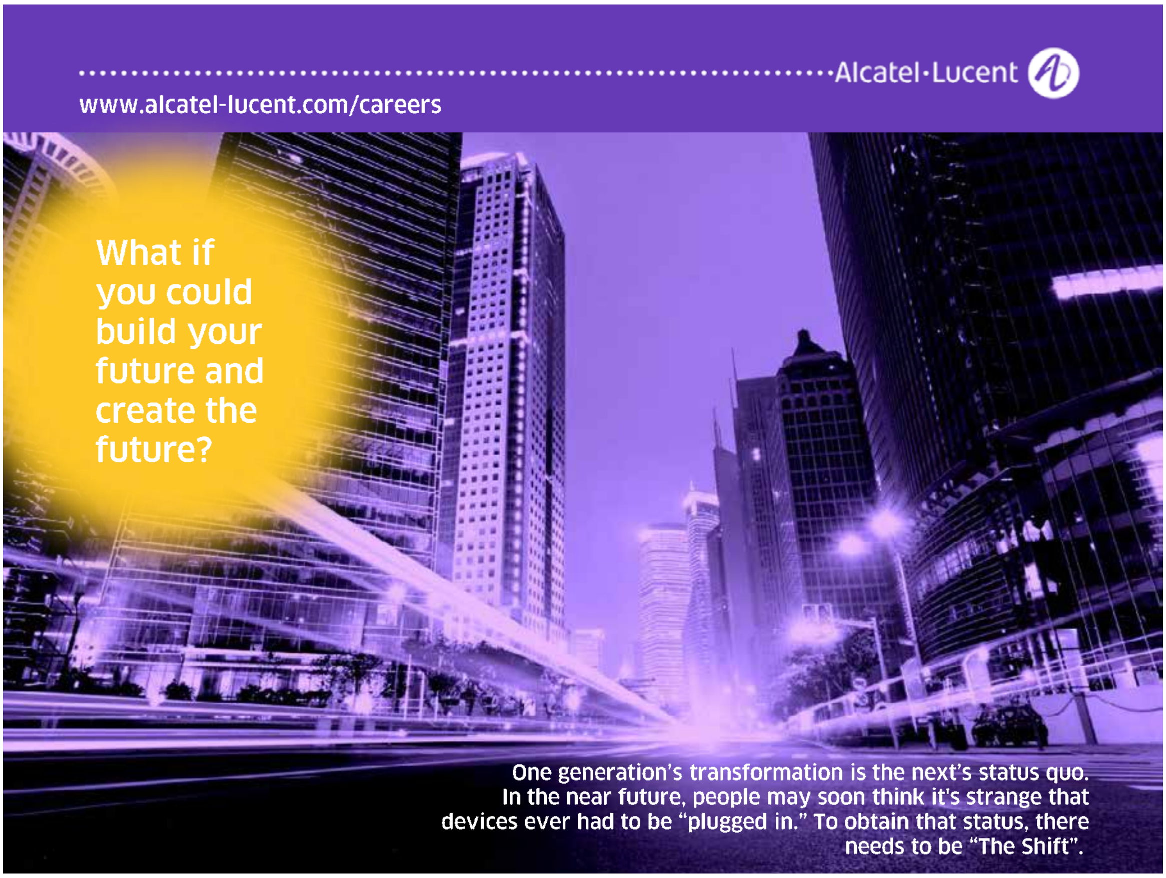


Figure 2.7: linear conjugated molecule H = grey, C = dark grey.



These molecules are important biologically for many functions including your ability to detect light within your eyes' retinas and for plant photosynthesis. Polyenes are also important industrial dyes. The quantum mechanics equation for the π-electrons in a "linear" conjugated polyene molecule has a wavefunction $\psi(x)$ that depends upon the position x along the length, L, of the molecule. The ideas of wavefunctions and quantum mechanics for such systems are covered early on in your Chemistry degree. The general equation that applies to all wave motion is given below.

$$\psi(x) = A\cos(k\,x) + B\sin(k\,x)$$

Where A, B and k are constants whose values need to be determined for the linear conjugated molecule. Find the constant k and any constraints that A or B may have using the following two boundary conditions. Firstly, when $x = 0$ then $\psi(0) = 0$ and secondly, when $x = L$ then $\psi(L) = 0$.

Jump to Solution 10 (see page 48)

2.1.11 Question 11: Molecular Structure

The water molecule has an O–H bond distances of 0.9687×10^{-10} m and the distance between the two hydrogen atoms is 1.5391×10^{-10} m. Calculate the H–O–H bond angle.

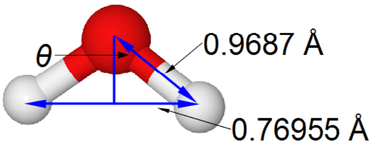


Figure 2.8: water O = red, H = grey.

Jump to Solution 11 (see page 49)

2.1.12 Question 12: Weak Acids

Ethanoic acid (acetic acid) is a weak acid which dissociates in water.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

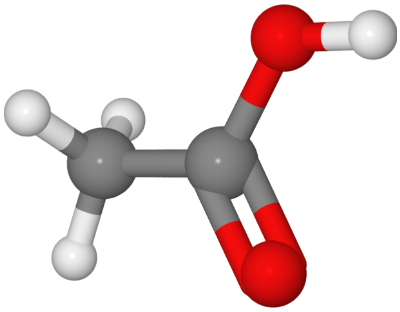


Figure 2.9: ethanoic acid (acetic acid) O = red, H = grey, C = dark grey.

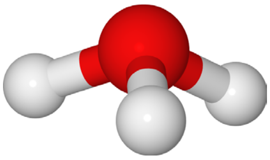


Figure 2.10: H_3O^+ hydronium ion (hydroxonium ion) O = red, H = grey.

An acid has an acidity constant K_a which is similar to an equilibrium constant K'_a

$$K'_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

Where each of the terms in square brackets have been divided by the standard concentration $c^o = 1$ mol L^{-1} and so the units cancel out to give the pure number, dimensionless "concentrations". The concentration of the solvent, water, $[H_2O]$ is approximately constant and is incorporated into the acidity constant K_a' to give

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

Acetic acid has an acidity constant $K_a = 1.8\times10^{-5}$. Calculate the hydronium ion concentration $[H_3O^+]$ for a 0.15 mol L^{-1} solution of acetic acid? We can tackle this chemical problem by saying the fraction of acid dissociated at equilibrium is x. For each molecule of acid that dissociates it gives an equal number of acetate anions and hydronium cations. So at equilibrium the tricky chemical problem has been reduced to solving the quadratic equation using the quadratic formula.

$$1.8\times10^{-5} = \frac{x^2}{0.15-x}$$

Jump to Solution 12 (see page 50)

2.1.13 Question 13: The Synthesis of Ammonia

Ammonia is an important industrial chemical.

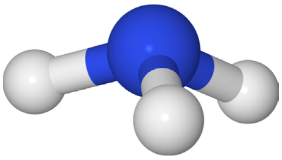


Figure 2.11: ammonia N = blue, H = grey.

Ammonia is synthesized using the equilibrium reaction where the reactant and products are in the gas-phase.

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

Its makes sense to use the partial pressures of the gases to define an equilibrium constant K_p. The reaction of forming ammonia from its elements has an equilibrium constant of $K_p = 977$ at a particular temperature.

$$K_p = \frac{\left(\dfrac{p_{NH_3}}{p^o}\right)^2}{\left(\dfrac{p_{N_2}}{p^o}\right)\left(\dfrac{p_{H_2}}{p^o}\right)^3} = 977$$

K_p is given in terms of the partial pressures of the reactants and products in pascals where each partial pressure is divided by the standard pressure of $p^o = 1\times10^5$ Pa = 1 bar and thus K_p is dimensionless. Each of the terms is raised to the power of its stoichiometric coefficient. Because the standard pressure $p^o = 1\times10^5$ Pa each of the p^o terms affect the value for K_p and we cannot make a simplification similar to the one we made for K_c(see section 1.2.3) but each of the K_p equations must be written in full with the p^o values included.

For our reaction we initially have 1.00×10^5 Pa pressure of N2 and 3.00×10^5 Pa of H_2 which are mixed, there being no NH_3 present and the mixture is allowed to come to equilibrium. If x is the fraction of a mole of N_2 which is lost due to the reaction then the equilibrium constant becomes

$$\begin{array}{ccccc} N_2 & + & 3H_2 & \rightleftharpoons & 2NH_3 \\ (1.00-x)\text{ Pa} & + & (3.00-3x)\text{ Pa} & \rightleftharpoons & 2x\text{ Pa} \end{array}$$

$$K_p = \frac{\left(\dfrac{2x\text{ Pa}}{1\times10^5\text{ Pa}}\right)^2}{\left(\dfrac{(1.00-x)\text{ Pa}}{1\times10^5\text{ Pa}}\right)\left(\dfrac{(3.00-3x)\text{ Pa}}{1\times10^5\text{ Pa}}\right)^3} = 977$$

Note that each time the reaction "occurs" we form two molecules of NH_3 hence the term $2x$. Likewise, each time the reaction occurs we lose 3 molecules of H_2 thus the term in the bracket is $(3.00 - 3x)$. Within each of the bracketted terms the units Pa cancel out so this is written as

$$K_p = \frac{\left(\dfrac{2x}{1\times10^5}\right)^2}{\left(\dfrac{1.00-x}{1\times10^5}\right)\left(\dfrac{3.00-3x}{1\times10^5}\right)^3} = 977$$

Firstly, calculate the fraction by solving for x using the quadratic formula. Secondly, using this value for x calculate the partial pressures of all the reactants and products. We can simplify the equation by taking out the common factors.

Jump to Solution 13 (see page 39)

2.2 Week 2 Tutorial Solutions

2.2.1 Solution 1: Energy of a Single Photon

$$c = \lambda \nu \qquad E = h\nu$$

The common variable in these two equations is the frequency, ν. The energy of a single photon is found by: (1) rearranging the first equation to get ν as the subject; (2) substituting this expression for ν into the second equation; and (3) then substituting in the physical quantities.

$$\nu = \frac{c}{\lambda} \qquad E = \frac{hc}{\lambda} \qquad E = \frac{(6.626\times10^{-34}\ \mathrm{J\ s})(2.998\times10^{8}\ \mathrm{m\ s^{-1}})}{427\times10^{-9}\ \mathrm{m}}$$

Note that in the calculation we have replaced nanometres by the base units metres in order that the units metres and seconds can cancel out.

$$\boxed{E = 4.652\times10^{-19}\ \mathrm{J}}$$

This is the energy of a *single* photon and it is incredibly *small*, the power of −19 is a very small fraction of a joule. In practice we normally only meet photons in enormous numbers (typically 10^{23} or more) which can give very large total energies, ~10s of kJ, of light energy.

Return to Question 1 (see page 29)

2.2.2 Solution 2: Rates of Chemical Reactions and Concentrations

$$v_{\mathrm{initial}} = k\frac{[\mathrm{A}]^2[\mathrm{B}]^3}{[\mathrm{C}]}$$

The final rate v_{final} is with all the above concentrations doubled and with the powers applying to the new *doubled* concentrations. The equation is cleaned up by taking the numerical factors outside the brackets.

$$v_{\mathrm{final}} = k\frac{[2\mathrm{A}]^2[2\mathrm{B}]^3}{[2\mathrm{C}]} = k\frac{4[\mathrm{A}]^2 8[\mathrm{B}]^3}{2[\mathrm{C}]} = 16k\frac{[\mathrm{A}]^2[\mathrm{B}]^3}{[\mathrm{C}]} = 16\,v_{\mathrm{initial}}$$

$$\boxed{\frac{v_{\mathrm{final}}}{v_{\mathrm{initial}}} = 16}$$

The ratio of the final rate of reaction v_{final} to the initial rate of reaction v_{initial} is 16. Doubling all the concentrations has made the reaction go 16 times faster!

Return to Question 2 (see page 29)

2.2.3 Solution 3: The Strength of an Ionic Crystal Structure

$$\Delta H^{\mathrm{o}}_{\text{lattice}} = -\Delta H^{\mathrm{o}}_{\text{formation}} + \Delta H^{\mathrm{o}}_{\text{sublimation}} + \frac{1}{2}\Delta H^{\mathrm{o}}_{\text{dissociation}} + \Delta H^{\mathrm{o}}_{\text{ionization}} + \Delta H^{\mathrm{o}}_{\text{electron gain}}$$

The equation is rearranged to give the electron gain enthalpy as the subject of the equation.

$$\Delta H^{\mathrm{o}}_{\text{electron gain}} = \Delta H^{\mathrm{o}}_{\text{lattice}} + \Delta H^{\mathrm{o}}_{\text{formation}} - \Delta H^{\mathrm{o}}_{\text{sublimation}} - \frac{1}{2}\Delta H^{\mathrm{o}}_{\text{dissociation}} - \Delta H^{\mathrm{o}}_{\text{ionization}}$$

Substituting the physical quantities for the symbols and splitting the equation over two lines for clarity gives,

$$\begin{aligned}\Delta H^{\mathrm{o}}_{\text{electron gain}} = {} & \left(+717\ \text{kJ mol}^{-1}\right) + \left(-437\ \text{kJ mol}^{-1}\right) - \left(+89\ \text{kJ mol}^{-1}\right) \\ & - \frac{1}{2}\left(+244\ \text{kJ mol}^{-1}\right) - \left(+418\ \text{kJ mol}^{-1}\right)\end{aligned}$$

Notice the difference between the mathematical *operations* of addition or subtraction as shown by plus or minus signs *outside* the brackets; and the positive or negative *values* of the physical quantities themselves shown by plus or minus *inside* the brackets. We can clean up the equation by removing the brackets and taking the common units out.

$$\Delta H^{\mathrm{o}}_{\text{electron gain}} = \left(+717 - 437 - 89 - \frac{1}{2}244 - 418 \right) \text{kJ mol}^{-1}$$

$$\Delta H^{\mathrm{o}}_{\text{electron gain}} = -349 \text{ kJ mol}^{-1}$$

Return to Question 3 (see page 30)

2.2.4 Solution 4: Kinetics of Isomerization

$$k_1[\mathrm{A}]^2 - k_2[\mathrm{A^*}][\mathrm{A}] - k_3[\mathrm{A^*}] = 0$$

The intermediate concentration [A*] is obtained as the subject by: (1) moving the term which does *not* involve [A*] to the right hand side by subtracting $k_1[\mathrm{A}]^2$ from both sides; (2) multiplying throughout by −1 to make all three terms positive; (3) taking [A*] outside the two terms on the left hand side; and finally (4) dividing left and right by (k_2[A] + k_3) and cancelling out top and bottom of any *single* term.

$$-k_2[\mathrm{A^*}][\mathrm{A}] - k_3[\mathrm{A^*}] = -k_1[\mathrm{A}]^2 \qquad k_2[\mathrm{A^*}][\mathrm{A}] + k_3[\mathrm{A^*}] = k_1[\mathrm{A}]^2$$

$$[\mathrm{A^*}]\left(k_2[\mathrm{A}] + k_3\right) = k_1[\mathrm{A}]^2$$

$$[\mathrm{A^*}] = \frac{k_1[\mathrm{A}]^2}{k_2[\mathrm{A}] + k_3}$$

We *cannot* cancel out the variable [A] top and bottom in the final equation because the denominator has a *plus sign* in it (the same would be true if it had had a *minus sign*) and so the denominator consists of two separate terms, *not* one single term. You can show this is true by examining the numeric example below.

$$\frac{2}{2\times3+3} = \frac{2}{9} \qquad \frac{2}{2\times3+3} \neq \frac{1}{6}$$

Return to Question 4 (see page 31)

2.2.5 Solution 5: Enthalpy of Combustion of Benzene

$$\Delta H^{\mathrm{o}}_{\mathrm{comb}} = 6\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{CO_2}) + 3\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{H_2O}) - \left(\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6}) + \frac{15}{2}\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{O_2})\right)$$

In order to not get lost in the algebra: (1) expand out the bracket on the right hand side;

$$\Delta H^{\mathrm{o}}_{\mathrm{comb}} = 6\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{CO_2}) + 3\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{H_2O}) - \Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6}) - \frac{15}{2}\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{O_2})$$

(2) take $\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6})$ over to the left hand side by adding $\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6})$ to both sides of the equation and cancelling out where possible;

$$\Delta H^{\mathrm{o}}_{\mathrm{comb}} + \Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6}) = 6\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{CO_2}) + 3\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{H_2O}) - \cancel{\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6})} - \frac{15}{2}\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{O_2}) + \cancel{\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6})}$$

$$\Delta H^{\mathrm{o}}_{\mathrm{comb}} + \Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6}) = 6\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{CO_2}) + 3\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{H_2O}) - \frac{15}{2}\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{O_2})$$

(3) take the enthalpy of combustion $\Delta H^{\mathrm{o}}_{\mathrm{comb}}$ to the right hand side by subtracting $\Delta H^{\mathrm{o}}_{\mathrm{comb}}$ from both sides and then cancelling out where possible.

$$\cancel{\Delta H^{\mathrm{o}}_{\mathrm{comb}}} + \Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6}) - \cancel{\Delta H^{\mathrm{o}}_{\mathrm{comb}}} = 6\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{CO_2}) + 3\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{H_2O}) - \frac{15}{2}\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{O_2}) - \Delta H^{\mathrm{o}}_{\mathrm{comb}}$$

(4) which then gives the heat of formation of benzene as the subject of the equation.

$$\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{C_6H_6}) = 6\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{CO_2}) + 3\,\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{H_2O}) - \frac{15}{2}\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{O_2}) - \Delta H^{\mathrm{o}}_{\mathrm{comb}}$$

Return to Question 5 (see page 32)

2.2.6 Solution 6: Hydrogen-Atom Spectroscopy

$$\bar{\nu} = R_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Rearranging to obtain n_2 as the subject of the equation is a bit more difficult than it may appear at first sight. (1) Expand out the bracket; (2) bring the term involving n_2 to the left hand side by adding R_{H}/n_2^2 to both sides and then cancelling out where possible;

$$\bar{\nu} = \frac{R_{\mathrm{H}}}{n_1^2} - \frac{R_{\mathrm{H}}}{n_2^2} \qquad \bar{\nu} + \frac{R_{\mathrm{H}}}{n_2^2} = \frac{R_{\mathrm{H}}}{n_1^2}$$

(3) nu-bar is moved to the right hand side by subtracting nu-bar from both sides and then cancelling out;

$$\frac{R_{\mathrm{H}}}{n_2^{\,2}} = \frac{R_{\mathrm{H}}}{n_1^{\,2}} - \bar{\nu}$$

(4) bring the right hand side to a common denominator of n_1^2; (5) divide left and right by R_{H} and then cancel out on the left hand side of the equals sign but *not* on the right hand side because of the minus sign, here the numerator consists of two terms; (6) take reciprocals on both sides; (7) take square root of both sides.

$$\frac{R_{\mathrm{H}}}{n_2^{\,2}} = \frac{R_{\mathrm{H}} - n_1^{\,2}\bar{\nu}}{n_1^{\,2}} \qquad \frac{1}{n_2^{\,2}} = \frac{R_{\mathrm{H}} - n_1^{\,2}\bar{\nu}}{n_1^{\,2}R_{\mathrm{H}}} \qquad n_2^{\,2} = \frac{n_1^{\,2}R_{\mathrm{H}}}{R_{\mathrm{H}} - n_1^{\,2}\bar{\nu}}$$

$$n_2 = \sqrt{\frac{n_1^{\,2}R_{\mathrm{H}}}{R_{\mathrm{H}} - n_1^{\,2}\bar{\nu}}}$$

Which is the correct equation with n_2 as the subject, however, you may have realized that n_1 in the numerator can be square rooted and taken outside the bracket to give an equally correct version. On the other hand n_1 in the denominator *cannot* be square rooted because of the minus sign, as the denominator is made up of two terms which must both be treated equally.

$$\boxed{n_2 = n_1\sqrt{\frac{R_H}{R_H - n_1{}^2\bar{v}}}}$$

Return to Question 6 (see page 32)

2.2.7 Solution 7: Chemical Equilibrium and Concentration Calculations

Note that the HI concentration 2*x* is *all* squared, it is *not* $2x^2$. Writing the denominator as a square term allows us to then take the square root of both sides.

$$K_c = \frac{[2x]^2}{[2-x][2-x]} = 55.64$$

$$K_c = \frac{[2x]^2}{[2-x]^2} = 55.64 \qquad \sqrt{K_c} = \frac{[2x]}{[2-x]} = \sqrt{55.64}$$

This is solved by: (1) multiplying left and right of the equals sign by [2 – *x*] and cancelling out within a single term; (2) then multiplying out the bracket;

$$\frac{[2x]}{[2-x]} = 7.459 \qquad [2x] = 7.459[2-x] \qquad 2x = 14.918 - 7.459x$$

(3) taking 7.459*x* over to the left hand side: (4) finally solve for *x*. In this example the two roots of the quadratic are the same so there is no choice for the “chemically sensible” root.

$$2x + 7.459x = 14.918 \qquad 9.459x = 14.918$$

$$\boxed{x = 1.577}$$

Thus the final equilibrium concentrations are

$$\boxed{\begin{aligned} c_{H_2} &= [H_2]\text{ mol L}^{-1} = (2-x)\text{ mol L}^{-1} = 0.423\text{ mol L}^{-1} \\ c_{I_2} &= [I_2]\text{ mol L}^{-1} = (2-x)\text{ mol L}^{-1} = 0.423\text{ mol L}^{-1} \\ c_{HI} &= [HI]\text{ mol L}^{-1} = 2x\text{ mol L}^{-1} = 3.154\text{ mol L}^{-1} \end{aligned}}$$

Return to Question 7 (see page 34)

2.2.8 Solution 8: Crystal Structures by X-Ray Diffraction

Rearrange the Bragg equation so that *d* is the subject and then substitute in the values of the variables.

$$n\lambda = 2d\sin(\theta) \qquad d = \frac{n\lambda}{2\sin(\theta)}$$

$$d = \frac{1\times 0.154\ \text{nm}}{2\sin\left(11^{\text{o}}\right)}$$

$$d = 0.404\ \text{nm}$$

Note that we do not need to change the units to metres, they may be left as nanometres (nm) but *whichever* unit of length is used it will need to have been inserted in the equation in order to know the units of the lattice spacing.

Return to Question 8 (see page 35)

2.2.9 Solution 9: Polymer Chemistry

$$r^2 = N l^2 \frac{1-\cos(\theta)}{1+\cos(\theta)}$$

Substituting in the values of the parameters for the variables gives

$$r^2 = \left(5\times 10^3\right)(154\ \text{pm})^2 \frac{1-\cos\left(109.5^{\text{o}}\right)}{1+\cos\left(109.5^{\text{o}}\right)} = 2.374\times 10^8\ \text{pm}^2$$

$$r = 1.5408\times 10^4\ \text{pm}$$

Average end-to-end distance for the polymer $r = 1.5408\times 10^4$ pm which is much less (~2%) of the stretched out “linear” length of polymer, 77×10^4 pm. Macromolecules, both natural and synthetic, will be covered in detail in your Chemistry lectures. Also it was not necessary to convert to metres, *but* it was necessary to have the units of the length in the equation.

Return to Question 9 (see page 35)

2.2.10 Solution 10: Conjugated Molecules and Quantum Mechanics

$$\psi\left(x\right) = A\cos\left(k\,x\right) + B\sin\left(k\;x\right)$$

The sin and cos are in radians. At the left hand end of the polyene molecule where $x = 0$, $\psi(0) = 0$ but we have $\cos(0) = 1$ and $\sin(0) = 0$. So the sine function fits with the quantum mechanics but the cosine does not. Hence in order to remove the cosine term from the general wave equation we must set $A = 0$. The general wavefunction becomes modified to

$$\psi\left(x\right) = B\sin\left(k\,x\right)$$

At the right hand end of the polyene molecule where $x = L$, $\psi(L) = 0$ and so $\sin(kL) = 0$.. This means kL must be equal to π or an integral number n of π where $n = 1, 2.\ 3, \cdots$ is a quantum number. In general, quantization arises because of the fulfilling of "boundary conditions" such as the ones in this question. We rearrange the sine angle equation $kL = n\pi$ to give the value of the previously unknown constant k.

$$k\,L = n\pi \qquad k = \frac{n\pi}{L}$$

Finally we have the wavefunction for the particle (the π-electrons) in a 1-dimensional box (the polyene conjugated molecule).

$$\boxed{\psi(x) = B\sin\left(\frac{n\pi x}{L}\right)}$$

We have found the constants $A = 0$ and $k = n\pi/L$ and the only constant that has yet to be found is B. The value of the constant B is calculated in section 8.2.2 this book. Fig. 2.12 shows the shape (and the relative energies) of the wavefunctions for a particle in a 1-dimensional box.

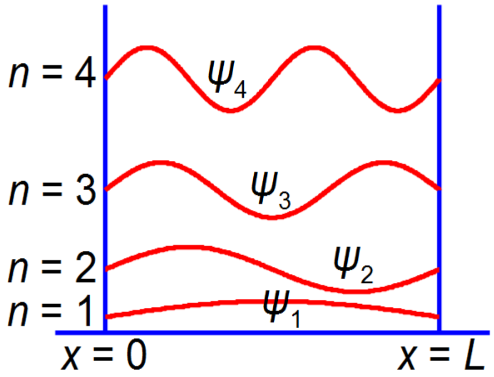


Figure 2.12: wavefunctions for a particle in a 1-dimensional box.

Return to Question 10 (see page 48)

2.2.11 Solution 11: Molecular Structure

The water molecule forms an equilateral triangular structure. We can then bisect the H–O–H angle to make two right angled triangles, the right hand triangle is drawn in Fig. 2.13. As this is now a right angled triangle we can use trigonometric functions where θ is the *half* angle for H–O–H. The distance multiple of 10^{-10} m is called an ångstrom with the symbol Å, it is a common and convenient unit used by Chemists as it is of the order of bond distances and atomic radii.

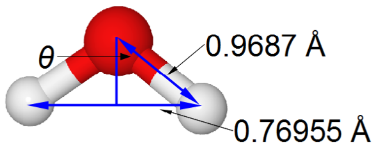


Figure 2.13: trigonometry of half of the water molecule.

$$\sin(\theta) = \frac{0.76955\ \text{Å}}{0.9687\ \text{Å}} = 0.79442 \qquad \theta = \sin^{-1}(0.79442) = 52.60^{\circ}$$

But as this is only half of the water bond angle, the bond angle is

$$\boxed{\mathrm{H}-\hat{\mathrm{O}}-\mathrm{H} = 105.2^{\circ}}$$

Jump to Question 11 (see page 37)

2.2.12 Solution 12: Weak Acids

$$1.8\times 10^{-5} = \frac{x^2}{0.15 - x}$$

The fraction of acid lost in going to the equilibrium, *x*, is found by solving the quadratic equation by: (1) multiplying both sides of the equation by the right hand denominator and cancelling out in any single term; (2) multiplying out the bracket;

$$\left(1.8\times 10^{-5}\right)\left(0.15 - x\right) = x^2 \qquad \left(2.7\times 10^{-6}\right) - \left(1.8\times 10^{-5}\,x\right) = x^2$$

(3) rearranging to the form of a standard quadratic equation; (4) the standard quadratic is solved using the quadratic formula where the symbols have their conventional meanings.

$$x^2 + \left(1.8\times 10^{-5}\right)x - \left(2.7\times 10^{-6}\right) = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-\left(1.8\times 10^{-5}\right) \pm \sqrt{\left(1.8\times 10^{-5}\right)^2 - 4\times 1\times\left(-2.7\times 10^{-6}\right)}}{2\times 1}$$

$$x = \frac{-\left(1.8\times 10^{-5}\right) \pm \sqrt{\left(3.24\times 10^{-10}\right) + \left(1.08\times 10^{-5}\right)}}{2}$$

Note the change of sign to the second term within the square root and also the *large* difference in magnitude between b^2 and $4ac$. I will *temporarily* be keeping some extra significant figures in order to show the effect of this relative difference in magnitudes between b^2 and $4ac$.

$$x = \frac{-\left(1.8\times 10^{-5}\right) \pm \sqrt{1.0800324\times 10^{-5}}}{2} = \frac{-\left(1.8\times 10^{-5}\right) \pm \left(3.286\times 10^{-3}\right)}{2}$$

Once we have taken the square root of the second term in the numerator then we only need to retain a sensible number of 4 or 5 significant figures. So which value of *x* applies in this question? Remember that *x* is the *fraction* of acetic acid that has dissociated. A fraction is a *positive* number of less than one. Another way of looking at this is that you cannot have a negative concentration, thus the chemically correct result is

$$c_{\mathrm{H_3O^+}} = x\ \mathrm{mol\ L^{-1}} = 1.6\times 10^{-3}\ \mathrm{mol\ L^{-1}}$$

Note: even though some of the data is only given to 2 significant figures it is necessary in order to not lose accuracy in the intermediate steps to carry out the calculation to 4 or 5 significant figures and before the square root is taken to 8 significant figures due to the *large* difference in the orders of magnitude of b^2 and $4ac$.

Although not part of the question, for the 0.15 mol L^{-1} acetic acid solution, this concentration of H_3O^+ corresponds to a pH = 2.8.

Jump to Question 12 (see page 37)

2.2.13 Solution 13: The Synthesis of Ammonia

$$K_p = \frac{\left(\frac{2x}{1\times10^5}\right)^2}{\left(\frac{1.00-x}{1\times10^5}\right)\left(\frac{3.00-3x}{1\times10^5}\right)^3} = 977$$

$$K_p = \frac{(2x)^2}{(1.00-x)(3.00-3x)^3}\times\frac{1}{\left(1/(1\times10^5)\right)^2} = 977$$

$$K_p = \frac{(2x)^2}{(1.00-x)(3.00-3x)^3} = 977\times\left(1/(1\times10^5)\right)^2$$

The equilibrium equation may be solved for x by: (1) taking out the common factor of $(1.00 - x)$ in the denominator and also squaring in the numerator; (2) collecting the $(1.00 - x)$ common factors together;

$$K_p = \frac{4x^2}{(1.00-x)\times3.00^3\times(1.00-x)^3} = 977\times10^{-10} \qquad K_p = \frac{4x^2}{(3.00^3)\times(1.00-x)^4} = 977\times10^{-10}$$

(4) cubing the 3.00 and rearranging the numerical factors;

$$K_p = \frac{4}{27}\frac{x^2}{(1.00-x)^4} = 977\times10^{-10} \qquad K_p = \frac{x^2}{(1.00-x)^4} = \frac{27\times977}{4}\times10^{-10}$$

(5) square rooting both sides of the equation;

$$\frac{x}{(1.00-x)^2} = \sqrt{\frac{27\times977}{4}\times10^{-10}} = 81.2081\times10^{-5}$$

(6) rearranging by multiplying by the denominator on both sides of the equation, then cancelling terms; (7) squaring the bracket; (8) multiplying out the bracket;

$$x = 81.2081\times10^{-5}(1.00-x)^2 \qquad x = 81.2081\times10^{-5}(1-2x+x^2)$$

$$x = (81.2081\times10^{-5}) - (162.4162\times10^{-5}x) + (81.2081\times10^{-5}x^2)$$

(9) rearranging into the "standard" quadratic form, note that "162" has become "163"; and (10) dividing by 81.2081×10^{-5} throughout to make the coefficients much more manageable.

$$(81.2081\times10^{-5}x^2) - (163.4162\times10^{-5}x) + (81.2081\times10^{-5}) = 0 \qquad x^2 - 2.0123x + 1 = 0$$

We can solve this quadratic equation using the quadratic formula,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad x = \frac{+2.0123 \pm \sqrt{4.04935 - 4.00000}}{2} \qquad x = \frac{+2.0123 \pm \sqrt{0.04935}}{2}$$

$$x = \frac{+2.0123 \pm 0.2221}{2} \qquad x = 1.1172 \quad \text{and} \quad x = 0.8951$$

As the mole fraction must be positive and *less than one* then $x = 0.8951$ is the chemically correct result. This gives the three equilibrium partial pressures as

$$\begin{aligned} p_{N_2} &= (1-x)\times 10^{-5}\ \text{Pa} = (1-0.8951)\times 10^{-5}\ \text{Pa} = 0.1049\times 10^{-5}\ \text{Pa} = 0.1049\ \text{bar} \\ p_{H_2} &= (3-3x)\times 10^{-5}\ \text{Pa} = (3-(3\times 0.8951))\times 10^{-5}\ \text{Pa} = 0.3147\times 10^{-5}\ \text{Pa} = 0.3147\ \text{bar} \\ p_{NH_3} &= (2x)\times 10^{-5}\ \text{Pa} = (2\times 0.8951)\times 10^{-5}\ \text{Pa} = 1.7902\times 10^{-5}\ \text{Pa} = 1.7902\ \text{bar} \end{aligned}$$

I have deliberately carried out the calculation in Pa but it looks clumsy. If, however, you work in bar where 1 bar = 1×10^5 Pa then the arithmetic looks cleaner.

Return to Question 13 (see page 39)

3 Week 3: Chemistry, Logarithms and Exponentials

3.1 Summary of Logs, Exponentials, and Acid-Base Equilibrium

Although hyperbolic functions may be part of your first year Maths syllabus, they have little *direct* chemical application, and so I have not included any contrived examples. You should nevertheless revise and understand hyperbolic functions for your Maths exam *if* they are part of your particular course.

This material should be completed in 1 week, and I thought it would be perhaps convenient for you to have a summary here about logs, exponentials and acid-base equilibrium.

3.1.1 Definition of a Logarithm

$$b^c = a \qquad b \text{ must be greater than 1 then} \qquad c = \log_b(a)$$

We say that c is the log to the base b of a. Here are two examples which are familiar from arithmetic.

$$10^2 = 100 \qquad 2 = \log_{10}(100) \qquad \text{and} \qquad 5^3 = 125 \qquad 3 = \log_5(125)$$

3.1.2 Rules of Logs

$$\log_a(x\,y) = \log_a(x) + \log_a(y) \qquad \log_a\left(\frac{x}{y}\right) = \log_a(x) - \log_a(y) \qquad \log_a(x^n) = n\log_a(x)$$

3.1.3 Additional rules

These are just special cases of the general rules above.

$$\log_a(a) = 1 \qquad \log_a(a^x) = x \qquad a^{\log_a(x)} = x \qquad \log_a(b) = \frac{1}{\log_b(a)}$$

3.1.4 Logs to base 10 and logs to base e

Logs to base 10 are used in science and engineering to express either very large numbers or very small numbers and are normally written as "log" without a 10 subscript, they are called "logs" or "common logs". Large numbers have positive powers *e.g.* 10^{23} and very small numbers have negative powers *e.g.* 10^{-34}.

Logs to base e are normally written as "ln" rather than $\log_e$ and they are called "natural logs" or "ln". They are important for their Maths properties which model many natural phenomena, hence they appear very often in science and engineering. The natural number e comes from the series below.

$$\mathrm{e}^{x} = 1 + x + \frac{x^{2}}{2!} + \frac{x^{3}}{3!} + \frac{x^{4}}{4!} + \cdots$$

The symbol "…" means "continues on for ever" and is called an "ellipsis". The symbol "!" means the factorial of the preceding number. For the special case when $x = 1$ we have

$$\mathrm{e} = 1 + 1 + \frac{1}{2!} + \frac{1}{3!} + \frac{1}{4!} + \cdots = 2.7182819\cdots$$

Note that e is a number and it is fixed, it is *not* a variable. This is similar to π or any other number *e.g.* 10 or 3.6, so it is not written in italic but upright roman script. In science and engineering we quite often find equations with e^{-x} in them, this is just a special case of e^{x} which alternates the sign of the terms for even and odd power of x.

$$\mathrm{e}^{-x} = 1 - x + \frac{x^{2}}{2!} - \frac{x^{3}}{3!} + \frac{x^{4}}{4!} - \cdots$$

$y = \mathrm{e}^{x}$ may also be written as $y = \exp(x)$ with "exp" *all in lower case*. This exp notation may be used for greater clarity particularly in printed material. An example from Chemistry is the Arrhenius equation $k = A\mathrm{e}^{-Ea/RT}$ which can also be written as $k = A\ \exp(-E_{\mathrm{a}}/RT)$. Be careful in using calculators as they sometimes have a key marked EXP, *all capitals*, which means "multiply by 10 raised to the power", which you then enter the power into the calculator.

3.1.5 Indicial Equations

$$12^{2x} = 35.4$$

The equation is called an indicial equation, the variable is present as an index or a power. To solve for x we firstly, take logs on both sides, secondly, from the rules of logs we can take the power down,

$$\log\left(12^{2x}\right) = \log\left(35.4\right) \qquad \left(2x\right)\times\log\left(12\right) = \log\left(35.4\right)$$

and finally now evaluating the logs gives.

$$\left(2x\right)\times 1.07918 = 1.54900 \qquad x = 0.71768$$

3.1.6 Acid-Base Equilibrium

The concentrations of H^+ and OH^- are very small in aqueous solution and involve many negative powers of ten in mol L^{-1}. Most humans are normally happier dealing with positive numbers that are in the range of 0 to a 100. The “p” part of the variables pH and pOH refers to the power or index of these small concentrations which are made more manageable by using logarithms. Taking the negative of the log converts the negative into a positive number. pH and pOH are written with upright roman script not as italics.

$$\mathrm{pH} = -\log_{10}\left[\mathrm{H}^+\right] \qquad \mathrm{pOH} = -\log_{10}\left[\mathrm{OH}^-\right]$$

We have an equilibrium constant for the self-ionization of water or the autoprotolysis of water

$$\mathrm{H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-}$$

This has an equilibrium constant K_c

$$K_c = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{OH}^-\right]}{\left[\mathrm{H_2O}\right]^2}$$

As the concentration of the solvent, water, is approximately constant we may combine the $[H_2O]^2$ with K_c to give K_W the autoprotolysis (or ionization) constant of water

$$K_W = [H_3O^+][OH^-] = K_c \times [H_2O]^2$$

The autoprotolysis constant of water is usually written in terms of proton and hydroxide ion concentrations

$$K_W = [H^+][OH^-]$$

K_W is the ionization constant for water and at 25°C, $K_W = 1 \times 10^{-14}$ (K_W is temperature dependent). From this definitions we can derive pK_W where pK_W is defined as minus the log of K_W.

$$pK_W = -\log_{10}(K_W) \qquad pK_W = pH + pOH = 14.000$$

For an acid we can define an acid dissociation constant K_a and a corresponding pK_a. Again incorporating the approximately constant solvent concentration $[H_2O]$ into K_a and I have not bothered writing the water in the reaction,

$$\underset{\text{acid}}{HA} \rightleftharpoons H^+ + \underset{\text{base}}{A^-} \qquad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+][\text{base}]}{[\text{acid}]} \qquad pK_a = -\log_{10}(K_a)$$

$$pK_a = pH - \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

Rearranging the equation we obtain the Henderson-Hasselbalch equation which applies to weak acids and buffer solutions. Use these equations to answer the following three questions.

$$pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

3.2 Week 3 Tutorial Questions

3.2.1 Question 1: Acid-Base Equilibrium

The molar concentration of OH^- ions in a certain solution is 1.04×10^{-5} mol L^{-1}. Calculate the pOH and then the pH of the solution.

Jump to Solution 1 (see page 64)

3.2.2 Question 2: Acid-Base Equilibrium

Death occurs if the pH of human blood plasma changes by more than about ±0.4 from its normal value of about pH = 7.4, the "safe" range is from neutral to slightly alkaline. What is the corresponding range of molar concentrations of hydrogen ions for which human life can be sustained?

Jump to Solution 2 (see page 64)

3.2.3 Question 3: Acid-Base Equilibrium

To understand the actions of buffer solutions in Chemistry we use the Henderson-Hasselbalch equation. Calculate the pH of a buffer solution that is 0.027 mol L^{-1} with respect to aqueous NH_3 *i.e.* the [base] = 0.027 mol L^{-1} and 0.025 mol L^{-1} with respect to NH_4Cl for which ammonium chloride has a $pK_a = 9.25$. The ionic salt NH_4Cl is fully dissociated into NH_4^+ and Cl^- and NH_4^+ and is a weak acid and so[acid] = 0.025 mol L^{-1}.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

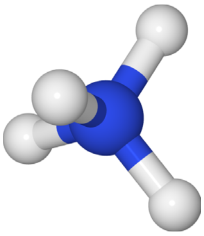


Figure 3.1: ammonium ion NH_4^+ with N = blue, H = grey.

Jump to Solution 3 (see page 64)

3.2.4 Question 4 First-order Kinetics

The concentration of the reactant in a first-order chemical reaction decreases with time as it is consumed to form products and the concentration of [A] varies with time as follows

$$[A] = [A]_0 e^{-kt}$$

Where $[A]_0$ is the initial concentration of the reactant at time $t = 0$, [A] is the concentration of the reactant at time t, and k is the rate constant for this particular reaction. Sketch the *shape* of the graph of $[A]/[A]_0$ plotted as the y-axis against time t plotted as the x-axis and label the two axes. You do *not* need to calculate anything. Fig. 3.2 shows the shape of a negative exponential curve.

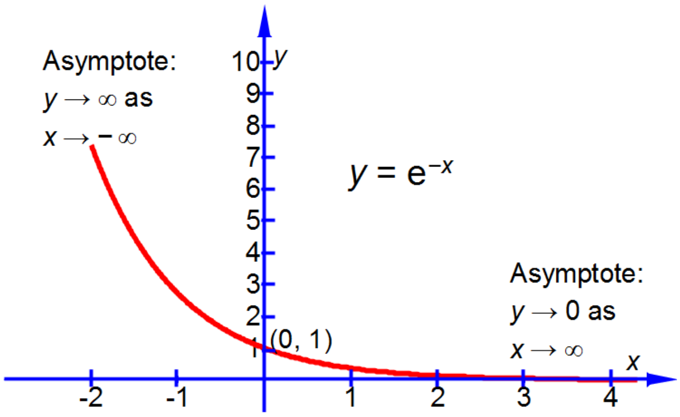


Figure 3.2: a negative exponential curve, the arrows mean "tends to".

Jump to Solution 4 (see page 65)

3.2.5 Question 5: First-order Kinetics

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

Write the natural-log form for a kinetic first-order reaction with ln([A]/[A]$_0$) as the subject.

Jump to Solution 5 (see page 65)

3.2.6 Question 6: First-order Kinetics

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

Sketch the graph which would give a straight line for a kinetic first-order reaction. Label the axes and give the meanings of the gradient and intercept.

Jump to Solution 6 (see page 66)

3.2.7 Question 7: First-order Kinetics

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

If a kinetic first-order reaction has a rate constant, $k = 1.83\times10^{-4}\ \mathrm{s}^{-1}$, calculate how long it would take for the concentration of reactant [A] to decrease from $3.25\times10^{-3}\ \mathrm{mol\ L}^{-1}$ to $2.18\times10^{-3}\ \mathrm{mol\ L}^{-1}$?

Jump to Solution 7 (see page 68)

3.2.8 Question 8: The Arrhenius Equation

The rate constant *k* of a chemical reaction increases with the absolute temperature *T*. This increase follows the equation below which is called the Arrhenius equation.

$$\boxed{k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}}$$

Where E_a is the activation energy for the reaction, *R* is the gas constant and *A* is called the pre-exponential factor which is a constant for a given reaction. Sketch the shape of the graph of *k* versus *T* labelling the axes.

Jump to Solution 8 (see page 68)

3.2.9 Question 9: The Arrhenius Equation

$$k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}$$

Write the Arrhenius equation in the form of natural-logs.

Jump to Solution 9 (see page 69)

3.2.10 Question 10: The Arrhenius Equation

$$k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}$$

Sketch the straight line graph with axes labelled for the Arrhenius equation. Give the meanings of the gradient and intercept.

Jump to Solution 10 (see page 70)

3.2.11 Question 11: The Arrhenius Equation

On your graph for Question 10, sketch the results for a linear plot for two different chemical reactions, one with large activation energy and the other with small activation energy, clearly label the two lines. Assume that both chemical reactions have the same value for A.

Jump to Solution 11 (see page 70)

3.2.12 Question 12: The Arrhenius Equation

The activation energy for the decomposition of hydrogen peroxide on a platinum catalyst is $E_\mathrm{a} = 48.9$ kJ mol^{-1} and $R = 8.314$ J K^{-1} mol^{-1}. Calculate the ratio of the new rate constant k_2 over the original rate constant k_1 of increasing the temperate from 20°C to 30°C?

Jump to Solution 12 (see page 71)

3.2.13 Question 13: The Nernst Equation

The following redox chemical reaction

$$\mathrm{Zn}(\mathrm{s}) + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}(\mathrm{s})$$

can be made into an electrochemical cell to derive electrical energy, Fig. 3.3.

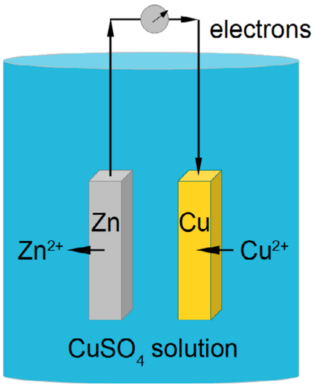


Figure 3.3: schematic diagram of a Daniell cell.

The cell is called the Daniell cell and was the power behind the telegraph systems in 1830s–1860s that connected up the world in the first high-speed communications system, a forerunner of the internet using the binary code (Morse code). The cell has a voltage difference between the zinc and copper metal electrodes which is given by the Nernst equation

$$E = E^{o} - \frac{RT}{nF}\ln\left(\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}\right)$$

Where E is the voltage under a given set of conditions, E^{o} is the standard voltage when all the concentrations are 1 mol L^{-1} (note we ignore the concentrations of the solid electrodes as they are constant), n is the number of electrons transferred in the reaction and in this case $n = 2$, R is the gas constant, T the temperature in kelvins, and F is a constant called the Faraday constant.

Calculate the concentration of $[\mathrm{Zn}^{2+}]$ for $E = 1.21$ V, $[\mathrm{Cu}^{2+}] = 0.1$ mol L^{-1}, $T = 298$ K, $n = 2$, $R = 8.314$ J K^{-1} mol^{-1}, $F = 96485$ J V^{-1} mol^{-1} = 96485 C mol^{-1} where C is a coulomb, and $E^{\mathrm{o}} = 1.10$ V.

Jump to Solution 13 (see page 72)

3.2.14 Question 14: Chemical Work at Constant Pressure

The ability of a chemical reaction to perform work at a constant pressure is given by the Gibbs energy ΔG^{o} where K is the equilibrium constant.

$$\Delta G^{\mathrm{o}} = -RT\ln(K)$$

Calculate ΔG^{o} for a reaction which has an equilibrium constant $K = 1.8\times10^{-5}$ at a temperature $T = 298$ K and $R = 8.314$ J K^{-1} mol^{-1} is the gas constant.

Jump to Solution 14 (see page 63)

3.2.15 Question 15: Radioactive Decay

Radioactive decay is a first-order chemical reaction which follows an exponential decay in the reactant, the radioactive element. Starting with an original number of radioactive atoms n_0 at time zero, the number of radioactive atoms left, n, after a certain time t is given by

$$n = n_{\mathrm{o}}\mathrm{e}^{-kt}$$

Where k is the rate constant for this decay reaction. The decay of $^{238}\mathrm{U}$ has a rate constant of $k = 1.54\times10^{-10}$ year^{-1} for the reaction

$$^{238}\mathrm{U} \longrightarrow \alpha + {}^{234}\mathrm{Th}$$

Where α is an alpha particle, a fast moving helium $^{4}\mathrm{He}^{2+}$ nucleus. Calculate the fraction of the uranium decayed after 4.51×10^{9} years, roughly the age of the Earth.

Jump to Solution 15 (see page 63)

3.3 Week 3 Tutorial Solutions

3.3.1 Solution 1: Acid-Base Equilibrium

$$\left[\mathrm{OH^-}\right] = 1.04\times10^{-5}\ \mathrm{mol\ L^{-1}} \qquad \mathrm{pOH} = -\log_{10}\left(1.04\times10^{-5}\right) = 4.98$$

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$

$$\mathrm{pH} = 14.00 - 4.98 = 9.02$$

This is an alkaline solution.

Return to Question 1 (see page 57)

3.3.2 Solution 2: Acid-Base Equilibrium

$$\begin{array}{lll} \text{Maximum pH} = 7.8 & 7.8 = -\log_{10}\left[\mathrm{H^+}\right]_{\max} & \left[\mathrm{H^+}\right]_{\max} = 10^{-7.8} \\ \text{Minimum pH} = 7.0 & 7.0 = -\log_{10}\left[\mathrm{H^+}\right]_{\min} & \left[\mathrm{H^+}\right]_{\min} = 10^{-7.0} \end{array}$$

From the definition of a logarithm we have $[\mathrm{H^+}] = 10^{-7.8}$. The easiest way of solving this on your calculator is to use "shift-log" (which is 10^x) then type −7.8 then equals. Take care to use "shift-log" = 10^x not "shift-ln" = e^x.

$$\left[\mathrm{H^+}\right]_{\max} = 1.58\times10^{-8}\ \mathrm{mol\ L^{-1}} \qquad \left[\mathrm{H^+}\right]_{\min} = 1.00\times10^{-7}\ \mathrm{mol\ L^{-1}}$$

Human blood covers only a small range of proton concentrations.

Return to Question 2 (see page 58)

3.3.3 Solution 3: Acid-Base Equilibrium

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log_{10}\left(\frac{[\mathrm{base}]}{[\mathrm{acid}]}\right) \qquad \mathrm{pH} = 9.25 + \log_{10}\left(\frac{0.027\ \mathrm{mol\ L^{-1}}}{0.025\ \mathrm{mol\ L^{-1}}}\right)$$

When evaluating this on the calculator, which can vary with the quality of their software, make sure that you use brackets, that is type log(0.027/0.025) = 0.03342 and *don't* type log 0.027/0.025 which may give −62.745 on low quality calculators and is incorrect. See section 3.1.2 for help with logs. This alkaline buffer has a pH given below.

$$\mathrm{pH} = 9.28$$

Return to Question 3 (see page 58)

3.3.4 Solution 4: First-order Kinetics

$$[\mathrm{A}] = [\mathrm{A}]_0 \mathrm{e}^{-kt} \qquad \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = \mathrm{e}^{-kt}$$

Remember that k is a constant for a given reaction at a fixed temperature and plotting $[\mathrm{A}]/[\mathrm{A}]_0$ versus t is a negative exponential and has the shape sketched in Fig. 3.4 which has an intercept at $[\mathrm{A}]/[\mathrm{A}]_0 = 1$ that is $[\mathrm{A}] = [\mathrm{A}]_0$ at $t = 0$. Note that using this non-linear plot it is *not* easy to deduce the rate constant k.

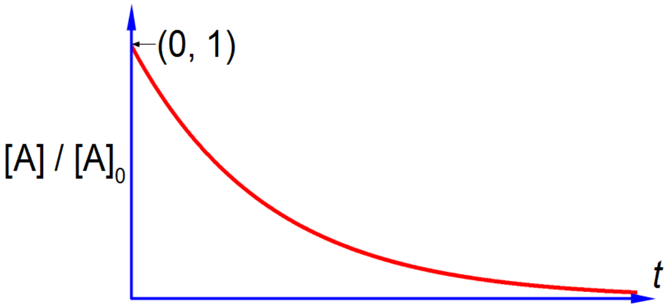


Figure 3.4: sketch of $[\mathrm{A}]/[\mathrm{A}]_0$ versus t for the Arrhenius equation.

Return to Question 4 (see page 58)

3.3.5 Solution 5: First-order Kinetics

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

From the first order kinetics equation: (1) take natural logs throughout; (2) expand out the right hand side which is the log of a product of two terms into the sum of the log of each term;

$$\ln[\mathrm{A}] = \ln\left([\mathrm{A}]_0 \mathrm{e}^{-kt}\right) \qquad \ln[\mathrm{A}] = \ln[\mathrm{A}]_0 + \ln\left(\mathrm{e}^{-kt}\right)$$

(3) the natural log of the exponential is just the exponent $-kt$; (4) move $\ln([\mathrm{A}]_0)$ to the left hand side by subtracting $\ln([\mathrm{A}]_0)$ from both sides; (5) convert the difference of two logs into the log of the ratio.

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt \qquad \ln[\mathrm{A}] - \ln[\mathrm{A}]_0 = -kt$$

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

Return to Question 5 (see page 59)

3.3.6 Solution 6: First-order Kinetics

Any of the following three graphs are correct and each of them are linear graphs allowing the rate constant to be easily found. From section 3.3.5 we have,

$$\begin{aligned} \ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) &= -k\,t \\ y &= m\,x + c \end{aligned}$$

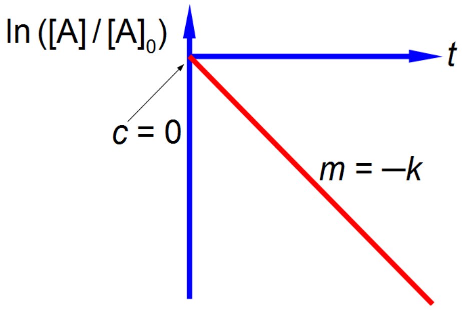


Figure 3.5: sketch of ln([A]/[A]$_0$) versus *t*.

From section 3.1.2 the rules of logs, we can invert the log function on the left hand side of the above (yellow) equation if the right hand side changes sign as in

$$\begin{array}{ccccc} \ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]}\right) & = & +kt & & \\ y & = & mx & + & c \end{array}$$

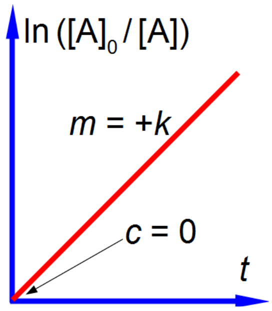


Figure 3.6: sketch of ln([A]$_0$/[A]) versus *t*.

An intermediate stage in section 3.3.5 allows a third and equally valid straight line graph to be plotted,

$$\begin{array}{cccc} \ln[\mathrm{A}] & = & \ln[\mathrm{A}]_0 & -kt \\ y & = & c & mx \end{array}$$

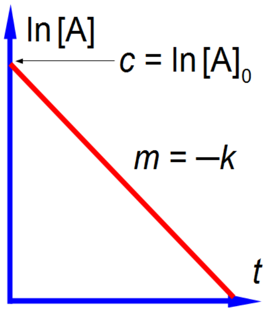


Figure 3.7: sketch of ln [A] versus *t*.

This plot has the advantage that you don't need to know the value of ln[A_0] which may be difficult to measure. Also we are not plotting a log of a *ratio* which may show only small variations in [A]/[A_0] for Fig. 3.5 or very large variations in [A_0]/[A] for Fig. 3.6.

Return to Question 6 (see page 60)

3.3.7 Solution 7: First-order Kinetics

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

Note that logs are dimensionless.

$$\ln\left(2.18\times10^{-3}\right) = \ln\left(3.25\times10^{-3}\right) - \left(1.83\times10^{-4}\,\mathrm{s}^{-1}\right)t$$

$$-6.1284 = -5.7291 - \left(1.83\times10^{-4}\,\mathrm{s}^{-1}\right)t \qquad -0.3993 = -\left(1.83\times10^{-4}\,\mathrm{s}^{-1}\right)t$$

$$t = \frac{-0.3993}{-1.83\times10^{-4}\,\mathrm{s}^{-1}}$$

$$t = 2.182\times10^{3}\,\mathrm{s} \qquad \text{or } 36.4 \text{ minutes}$$

Return to Question 7 (see page 60)

3.3.8 Solution 8: The Arrhenius Equation

$$k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}$$

From the Arrhenius equation one can plot k against T as in Fig. 3.8.

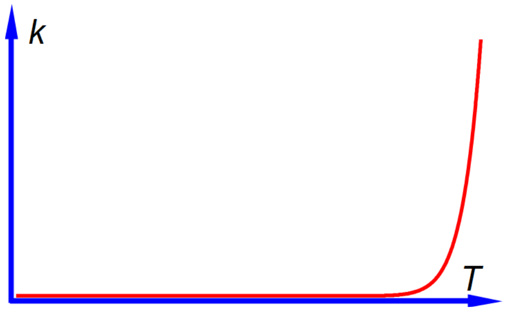


Figure 3.8: sketch of *k* against *T* for the Arrhenius equation.

In Fig. 3.8 it is difficult to read as at high temperatures a small change in T gives drastic changes in the rate constant k but at low temperatures a large change in T gives a negligible change in k. It would be much better if we can rearrange the Arrhenius equation to enable us to have a linear (straight line) graph.

Return to Question 8 (see page 60)

3.3.9 Solution 9: The Arrhenius Equation

$$k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}$$

We can go from the exponential form of the Arrhenius equation to the natural-log form by: (1) taking natural logs on both sides, (2) the log on the right is a product of two terms which can be separated as the sum of two logs, (3) the second term on the right is a natural-log of an exponential which is just equal to the exponent.

$$\ln(k) = \ln\left(A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}\right) \qquad \ln(k) = \ln(A) + \ln\left(\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}\right)$$

$$\boxed{\ln(k) = \ln(A) - \frac{E_\mathrm{a}}{RT}}$$

Return to Question 9 (see page 60)

3.3.10 Solution 10: The Arrhenius Equation

$$\ln(k) = \ln(A) - \frac{E_\mathrm{a}}{RT}$$

Rewriting the log form of the Arrhenius equation as below, helps us see that it is in the form of a straight line equation of the form $y = c + mx$

$$\begin{array}{ccccc} \ln(k) & = & \ln(A) & -\frac{E_\mathrm{a}}{R} & \frac{1}{T} \\ y & = & c & +m & x \end{array}$$

Hence plotting $\ln(k)$ as the y-axis and $1/T$ as the x-axis has the intercept $c = \ln(A)$ and the gradient $m = -E_\mathrm{a}/R$ this graph is called an *Arrhenius plot*.

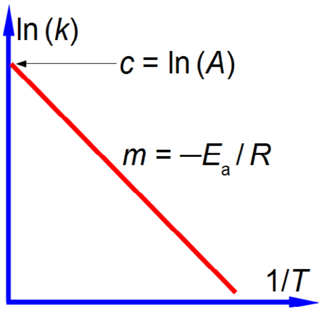


Figure 3.9: sketch of ln(k) versus (1/T) the Arrhenius Plot.

Return to Question 10 (see page 61)

3.3.11 Solution 11: The Arrhenius Equation

Fig. 3.10 shows that a reaction with a large E_a is *more* affected by changes in temperature than one with a small E_a (in the limit of zero activation energy the rate constant would be independent of temperature).

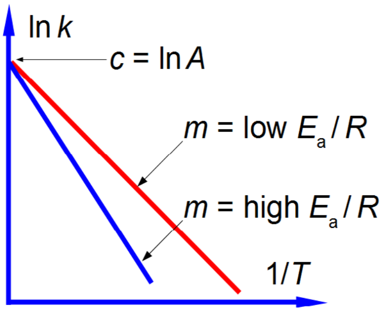


Figure 3.10: sketch of ln(k) versus (1/T) for high and low activation energies.

Return to Question 11 (see page 61)

3.3.12 Solution 12: The Arrhenius Equation

This increase in temperature for the Arrhenius equation is most easily handled using the logarithmic form of the Arrhenius equation, realizing that k and T are both variables whilst A and E_a are both constant for any given chemical reaction.

$$\ln(k_1) = \ln(A) - \frac{E_a}{RT_1} \qquad \ln(k_2) = \ln(A) - \frac{E_a}{RT_2}$$

(1) Subtracting the lower temperature T_1 equation from the higher temperature T_2 equation; and (2) substituting the physical quantities for the variables gives

$$\ln(k_2) - \ln(k_1) = \ln(A) - \ln(A) - \frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1}\right) \qquad \ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ln\left(\frac{k_2}{k_1}\right) = -\frac{48.9\times10^3\ \mathrm{J\ mol^{-1}}}{8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}}\left(\frac{1}{303.15\ \mathrm{K}} - \frac{1}{293.15\ \mathrm{K}}\right)$$

We note that the activation energy in kJ mol^{-1} must be converted to the base unit of J mol^{-1} in order to cancel out the units, and also that T must *always* be in kelvin.

$$\ln\left(\frac{k_2}{k_1}\right) = -(5882\ \mathrm{K})(3.299\times10^{-3}\ \mathrm{K^{-1}} - 3.411\times10^{-3}\ \mathrm{K^{-1}})$$

$$\ln\left(\frac{k_2}{k_1}\right) = -(5882\ \mathrm{K})(-0.112\times10^{-3}\ \mathrm{K^{-1}}) \qquad \ln\left(\frac{k_2}{k_1}\right) = 0.6588$$

The anti-log of 0.6588 (equivalent to finding $e^{0.6588}$) is found as "shift-ln" then 0.6588 on most calculators.

$$\frac{k_2}{k_1} = 1.9325$$

Thus for *this* particular reaction its rate constant has almost doubled and the reaction is going almost twice as fast for a 10°C rise in temperature from 20°C to 30°C.

Return to Question 12 (see page 61)

3.3.13 Solution 13: The Nernst Equation

$$E = E^{\circ} - \frac{RT}{nF} \ln\left(\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}\right)$$

The Nernst equation for the $\mathrm{Zn^{2+}/Cu^{2+}}$ redox reaction is solved for $[\mathrm{Zn^{2+}}]$ by: (1) substituting in the known variables; (2) rearranging the equation so that the term containing $[\mathrm{Zn^{2+}}]$ is the subject; (3) the exponential being evaluated as “shift-ln” on most calculators.

$$1.21\ \mathrm{V} = 1.10\ \mathrm{V} - \frac{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})}{2(96485\ \mathrm{J\ V^{-1}\ mol^{-1}})} \ln \frac{[\mathrm{Zn}^{2+}]}{(0.1\ \mathrm{mol\ L^{-1}})}$$

$$\frac{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})}{2(96485\ \mathrm{J\ V^{-1}\ mol^{-1}})} \ln \frac{[\mathrm{Zn}^{2+}]}{(0.1\ \mathrm{mol\ L^{-1}})} = 1.10\ \mathrm{V} - 1.21\ \mathrm{V}$$

$$\ln \frac{[\mathrm{Zn}^{2+}]}{(0.1\ \mathrm{mol\ L^{-1}})} = (-0.11\ \mathrm{V}) \frac{2(96485\ \mathrm{J\ V^{-1}\ mol^{-1}})}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})}$$

$$\ln \frac{[\mathrm{Zn}^{2+}]}{(0.1\ \mathrm{mol\ L^{-1}})} = -8.5675 \qquad \frac{[\mathrm{Zn}^{2+}]}{(0.1\ \mathrm{mol\ L^{-1}})} = \mathrm{e}^{-8.5675} = 1.9019 \times 10^{-4}$$

$$[\mathrm{Zn}^{2+}] = (1.9019 \times 10^{-4})(0.1\ \mathrm{mol\ L^{-1}})$$

$$[\mathrm{Zn}^{2+}] = 1.9019 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$$

As well as power sources such as batteries and fuel cells, electrochemical methods are commonly used in analytical chemistry for determining the concentrations of metal ions in drinking water, rivers, lakes, off-shore water, blood, drinks, food products, and in environmental pollution monitoring. Electrochemistry is also used in the industrial production of many important metals *e.g.* aluminium and magnesium.

Return to Question 13 (see page 61)

3.3.14 Solution 14: Chemical Work at Constant Pressure

$$\Delta G^{\circ} = -RT\ln\left(K\right) \qquad \Delta G^{\circ} = -\left(8.314 \text{ J K}^{-1}\text{ mol}^{-1}\right)\left(298\text{ K}\right)\ln\left(1.8\times10^{-5}\right)$$

$$\Delta G^{\circ} = -\left(8.314 \text{ J K}^{-1}\text{ mol}^{-1}\right)\left(298\text{ K}\right)\left(-10.925\right) = +2.7068\times10^{4}\text{ J mol}^{-1}$$

$$\Delta G^{\circ} = +27.1\text{ kJ mol}^{-1}$$

Note that we normally quote results in multiples of 10^3 or 10^{-3} and use the appropriate multiple symbol, here it is kilo with the symbol k. The equilibrium constant K is quoted to two significant figures and a variation in K of $\pm 0.1\times10^{-5}$ gives ΔG° with $\pm 0.14\text{ kJ mol}^{-5}$ hence the above final result.

Return to Question 14 (see page 63)

3.3.15 Solution 15: Radioactive Decay

Using the “exp” nomenclature for clarity

$$\frac{n}{n_o} = \exp\left(-k\,t\right) \qquad \frac{n}{n_o} = \exp\left(-1.54\times10^{-10}\text{ yr}^{-1}\right)\left(4.51\times10^{9}\text{ yr}\right)$$

$$\frac{n}{n_o} = 0.499$$

Thus during the lifetime of the Earth about half of the ^{238}U originally present has been converted to thorium-234 ^{234}Th which is itself unstable to fission reactions and decays further.

Return to Question 15 (see page 63)

4 Week 4: Experimental Data Analysis

As there is a lot of graph plotting in analysing experimental data, it would be useful to revise section 1.1.4 before commencing.

4.1 Week 4 Tutorial Questions

4.1.1 Question 1: Photoelectric Experimental Results

Light of various selected frequencies ν was directed at a sodium metal target inside a vacuum system. The kinetic energy of the ejected electrons E_{KE} was measured by the voltage required to stop them, this stopping voltage being then converted to units of joules. Fig. 4.1 is a schematic drawing of the experiment, it does not show the grid electrode to which the stopping voltage is applied for reasons of clarity.

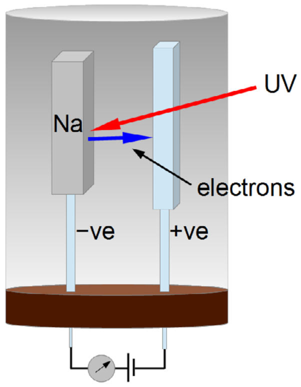


Figure 4.1: photoelectric schematic apparatus.

There is a minimum energy of the UV photon which must be used for a given metal for it to lose an electron, this minimum energy is called the "work function" of the metal Φ (upper case phi) the work function is the solid state equivalent to the ionization energy of a gas phase atom. The UV photon is annihilated when it is absorbed and its energy $h\nu$ is used to overcome the work function and eject the electron with any excess energy from the original photon appearing as the ejected electron's kinetic energy E_{KE}

$$h\nu = \Phi + E_{\mathrm{KE}}$$

A student took these experimental measurements of the photoelectric effect for sodium.

$E_{\mathrm{KE}}/\left(10^{-19}\ \mathrm{J}\right)$	2.70	1.77	1.23	0.26
$\nu/\left(10^{14}\ \mathrm{s}^{-1}\right)$	9.59	8.21	7.41	5.83

Firstly, manually plot the graph of E_{KE} against the ν (this is good practice for exams!). Secondly, does the data form a good straight line plot, *i.e.* is the energy of the ejected electrons proportional to the frequency of the light hitting the sodium metal target? Thirdly, determine the values of the gradient of the line, Planck's constant h. Fourthly, determine the work function Φ from the x-axis intercept (*not* the y-axis intercept).

Jump to Solution 1 (see page 78)

4.1.2 Question 2: Pressure-Volume Experimental Data for Carbon Dioxide

The volume, V litres, of one mole of CO_2 gas was measured as the pressure of p atmospheres (atm) was varied at a constant temperature of 313 K.

p/ atm	1	10	50	100	200	500
V / L	25.51	2.45	0.38	0.07	0.05	0.04

Manually plot p versus V and also plot $\log(p)$ against $\log(V)$. Comment upon which of the plots is most useful for displaying the data.

Jump to Solution 2 (see page 80)

4.1.3 Question 3: Experimental Arrhenius Plot

$$k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}$$

The Arrhenius equation was introduced in last week's questions. Firstly, using the following experimental data for the rate constants and temperatures draw a graph of $\ln(k/\mathrm{s}^{-1})$ versus $(1/T)\times(10^3\ \mathrm{K})$ the reciprocal of the pure number obtained by dividing the temperature by its unit kelvin, see section 1.1.4. Secondly, determine the values of A and E_a for this reaction. Thirdly, use the equation of the line from the graph to calculate the rate constants at 283 K (do *not* extrapolate the graph).

T/K	293	298	303	308	313	318	323
$k/\left(10^{-3}\ \mathrm{s}^{-1}\right)$	5.26	7.56	14.4	22.7	48.3	62.1	119

Jump to Solution 3 (see page 80)

4.1.4 Question 4: Experimentally Determining of the Order of a Chemical Reaction

The rate of a chemical reaction depends upon the rate constant and the concentrations of the reagents and products each raised to a power, the powers are called the *order* with respect to that compound. For example, if we consider a particular chemical reaction involving H_2 the rate of the reaction is

$$v = k\left[\mathrm{H}_2\right]^x$$

where v is the *rate of reaction*, k is the *rate constant* (don't get these two *different* terms confused) and x is the order with respect to H_2. The following data for the rate of reaction is given in terms of seconds and pressure in torr (1 bar = 750 Torr to three significant figures) the pressure is proportional to concentration at a constant T.

$v/\left(10^{-2}\ \mathrm{Torr\ s}^{-1}\right)$	4.20	3.40	2.60	2.05	1.65
p/Torr	400	316	248	196	155

Plot a log-log graph of the experimental data and assuming that the order x is either an integer or a half-integer for this reaction, determine x the order with respect to $[\mathrm{H}_2]$. Having determined the order x, find the rate constant for the reaction at the temperature T of the H_2 gas.

Jump to Solution 4 (see page 82)

4.1.5 Question 5: Vapour Pressure Data for a Liquid

The vapour pressure of the solvent above a liquid varies with temperature according to

$$\ln(p) = -\frac{\Delta H_{\text{vap}}}{RT} + B$$

where p is the vapour pressure; ΔH_{vap} is a measure of the energy required to evaporate a mole of the solvent (that is transform it from liquid to its gaseous form); T is the temperature in kelvin; and B is a constant. A student in the teaching lab obtained the following data which lists the measured vapour pressure of hexane in torr at various temperatures in °C up to its boiling point at 68.7°C. A torr (symbol Torr) is a convenient unit of pressure when using a mercury manometer with a ruler calibrated in millimetres even though it is non-SI (760 Torr = 101325 Pa = 1 atm). The temperatures are converted using 0°C = 273.15 K. Graphically determine ΔH_{vap}.

temp/°C	−53.9	−25	−2.3	15.8	49.6	68.7
p/Torr	1	10	40	100	400	760

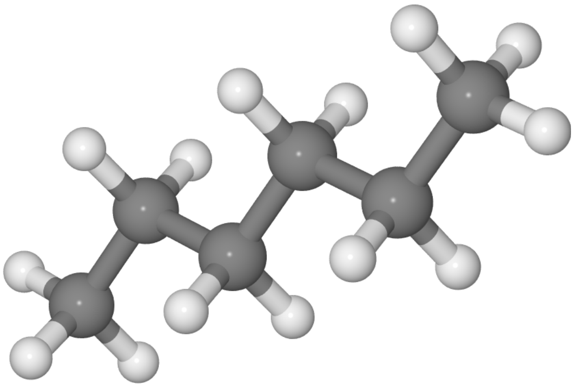


Figure 4.2: hexane H = grey and C = dark grey.

Jump to Solution 5 (see page 83)

4.2 Week 4 Tutorial Solutions

4.2.1 Solution 1: Photoelectric Experimental Results

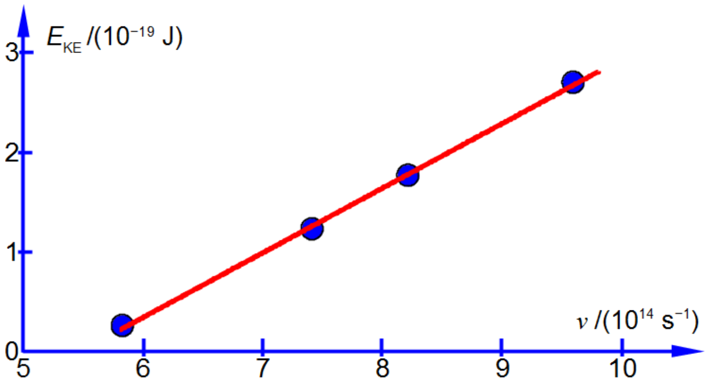


Figure 4.3: photoelectric experimental results.

There is a linear dependence of the kinetic energy of the ejected electron with the frequency of the light. There is a threshold frequency for the photoelectric effect. To find the equation of the line $y = mx + c$ by hand, we need to pick two points *on the line* and use their (x, y) coordinates, see section 1.1.4. Do not use the data points themselves else you are wasting your time drawing a graph! The two points of the line that I measured from the full sized manually drawn graph lead to the two simultaneous equations below.

$$\left(x_1, y_1\right) = \left(6.00\times10^{14}\,\mathrm{s}^{-1},\ 0.35\times10^{-19}\,\mathrm{J}\right) \qquad 0.35\times10^{-19}\,\mathrm{J} = m\left(6.00\times10^{14}\,\mathrm{s}^{-1}\right) + c$$
$$\left(x_2, y_2\right) = \left(9.00\times10^{14}\,\mathrm{s}^{-1},\ 2.31\times10^{-19}\,\mathrm{J}\right) \qquad 2.31\times10^{-19}\,\mathrm{J} = m\left(9.00\times10^{14}\,\mathrm{s}^{-1}\right) + c$$

Subtracting the two simultaneous equations gives

$$1.96\times10^{-19}\,\mathrm{J} = m\left(3\times10^{14}\,\mathrm{s}^{-1}\right) \qquad m = 6.53\times10^{-34}\,\mathrm{J\,s}$$

The student's value for Planck's constant from the gradient is

$$h = 6.53\times10^{-34}\,\mathrm{J\,s}$$

The accepted value for Planck's constant is $h = 6.626\times10^{-34}$ J to four significant figures. Adding the two simultaneous equations and using the student's value for m the student found the intercept

$$2.66\times10^{-19}\,\mathrm{J} = \left(6.53\times10^{-34}\,\mathrm{J\,s}\right)\left(15.00\times10^{14}\,\mathrm{s}^{-1}\right) + 2c \qquad c = -3.57\times10^{-19}\,\mathrm{J}$$

The student's equation of the straight line is

$$E_{\mathrm{KE}} = \left(6.53\times10^{-34}\,\mathrm{J\,s}\right)\nu - \left(3.57\times10^{-19}\,\mathrm{J}\right)$$

The intercept c is on the y-axis and we require the intercept on the x-axis *i.e.* the value of x when $y = 0$. So from the equation of the line we enter the value of $y = 0$.

$$0 = \left(6.53\times10^{-34}\,\mathrm{J\,s}\right)\nu_0 - \left(3.57\times10^{-19}\,\mathrm{J}\right) \qquad \nu_0 = \frac{3.57\times10^{-19}\,\mathrm{J}}{6.53\times10^{-34}\,\mathrm{J\,s}} \qquad \nu_0 = 5.47\times10^{14}\,\mathrm{s}^{-1}$$

The work function is the minimum photon energy required for electron emission, $\Phi = h\nu_0$

$$\Phi = \left(6.53\times10^{-34}\,\mathrm{J\,s}\right)\left(5.47\times10^{14}\,\mathrm{s}^{-1}\right) = 3.57\times10^{-19}\,\mathrm{J}$$

The accepted value for the work function of sodium metal is $\Phi = 3.78\times10^{-19}$ J, so the student's work function is inaccurate by about 6% and needs some improvement to either the apparatus or method.

Return to Question 1 (see page 74)

4.2.2 Solution 2: Pressure-Volume Experimental Data for Carbon Dioxide

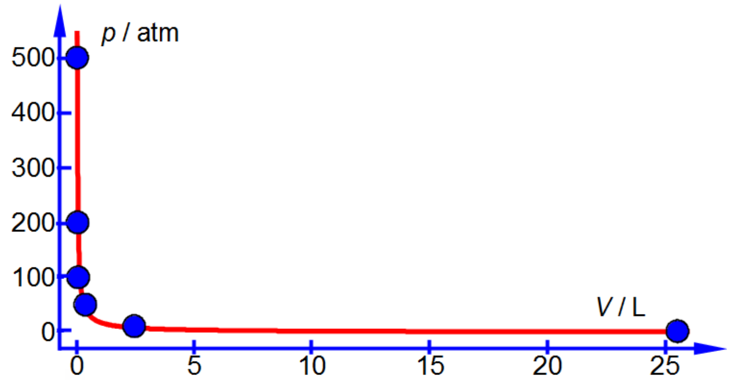


Figure 4.4: pressure against volume plot for CO_2.

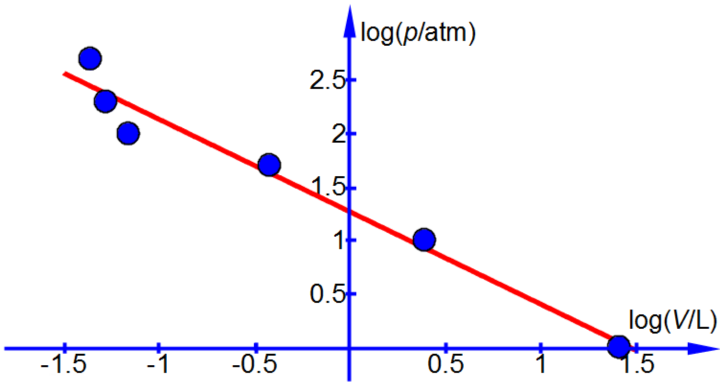


Figure 4.5: log(*p*) versus log(*V*) plot for CO_2.

The data covers a wide range of values and clearly the log-log plot allows the data to be viewed more clearly and it also would allow any "rogue" points in the experimental data to be noted for remeasuring.

Return to Question 2 (see page 75)

4.2.3 Solution 3: Experimental Arrhenius Plot

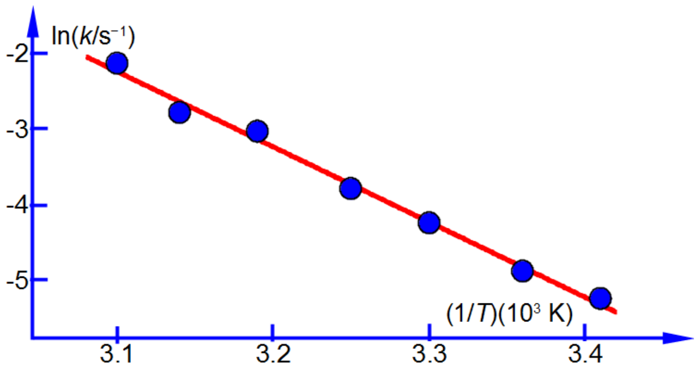


Figure 4.6: Arrhenius plot of rate constant and temperature data.

In Fig. 4.6 the Arrhenius plot is a straight line. From a full-sized manually-drawn version of Fig. 4.6 I obtained $y = -9.98x + 28.7$. The Arrhenius equation has a gradient $m = -E_a/R$ where R is the gas constant and E_a is the activation energy. So from the gradient we obtain the activation energy E_a we must also remember to include the units and their multiples of the axes in the calculation.

$$m = \frac{\ln\left(k/\mathrm{s}^{-1}\right)}{\frac{1}{T}\left(10^3\ \mathrm{K}\right)} = -9.98 \qquad m = \frac{\ln\left(k/\mathrm{s}^{-1}\right)}{\frac{1}{T}} = -9.98\times 10^3\ \mathrm{K} \qquad -\frac{E_a}{R} = -9.98\times 10^3\ \mathrm{K}$$

$$E_a = \left(9.98\times 10^3\ \mathrm{K}\right)\left(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\right) = 83.0\times 10^3\ \mathrm{J\ mol^{-1}}$$

$$E_a = 83.0\ \mathrm{kJ\ mol^{-1}}$$

The equation of the straight line in Fig. 4.6 has an intercept of $c = 28.7$ which for the Arrhenius equation is equal to $c = \ln(A)$. The intercept is on the y-axis and so the intercept will have the *same* units and any multiples there happens to be as the y-axis.

$$c = \ln\left(A/\mathrm{s}^{-1}\right) = 28.7 \qquad A/\mathrm{s}^{-1} = 2.91\times 10^{12}$$

$$A = 2.91\times 10^{12}\ \mathrm{s}^{-1}$$

To calculate the rate constant at $T = 283$ K then $(1/T) = (3.5336\times10^{-3}\ \mathrm{K}^{-1})$ and so $x = (3.5336\times10^{-3}\ \mathrm{K}^{-1})$ using the equation for the best line we can then calculate the corresponding value for $y = \ln(k/\mathrm{s}^{-1})$.

$$\ln\left(k/\mathrm{s}^{-1}\right) = \left(-9.98\times10^{3}\ \mathrm{K}\right)\left(3.5336\times10^{-3}\ \mathrm{K}^{-1}\right) + 28.7 = -6.57$$

$$k = 1.40\times10^{-3}\ \mathrm{s}^{-1}$$

Return to Question 3 (see page 76)

4.2.4 Solution 4: Experimental Determining of the Order of a Chemical Reaction

$$v = k\left[\mathrm{H}_2\right]^{x}$$

We will (1) take logs on both sides of the equation; (2) expand out the log of a product; and (3) bring the power of the log down.

$$\log(v) = \log\left(k\left[\mathrm{H}_2\right]^{x}\right) \qquad \log(v) = \log(k) + \log\left[\mathrm{H}_2\right]^{x}$$

$$\log(v) = \log(k) + x\log\left[\mathrm{H}_2\right]$$

This has the form of $y = c + mx$ with the $y = \log(v)$, the intercept $c = \log(k)$ the log of the rate of reaction, the gradient $m = x$ the order of the chemical reaction with respect to H_2 and $x = \log([H_2])$. Don't confuse the order of reaction x and the general variable x (as in x, y). Note this is written deliberately in terms of using x as the power because examiners are *sneaky* enough to try and confuse you!

$v/\left(10^{-2}\ \mathrm{Torr\ s}^{-1}\right)$	4.20	3.40	2.60	2.05	1.65
p/Torr	400	316	248	196	155

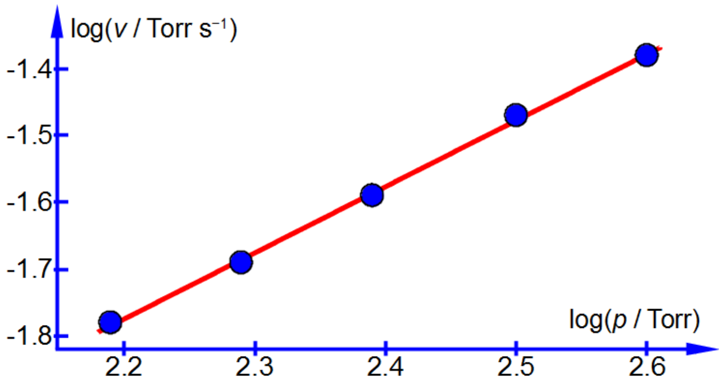


Figure 4.7: log of the rate of reaction versus log of the pressure.

The values of the gradient and intercept from a full size manual plot are

$$m = 0.9992 \qquad c = -3.9741$$

So $x = 0.9992$ which as the order for this reaction is expected to be an integer or half-integer, gives

$$x = 1.0 \text{ first-order}$$

Having determined x, we can now find the rate constant for the reaction at this temperature

$$c = \log\left(k/\mathrm{s}^{-1}\right) = -3.9741 \qquad k/\mathrm{s}^{-1} = 10^{-3.9741}$$

$$k = 1.06 \times 10^{-4}\ \mathrm{s}^{-1}$$

Return to Question 4 (see page 76)

4.2.5 Solution 5: Vapour Pressure Data for a Liquid

In order to have a straight line graph we construct a table for ln(p/Pa) and (1/T)(10^3 K).

temp/°C	−53.9	−25	−2.3	15.8	49.6	68.7
T/K	219.3	248.2	270.9	289.0	322.8	341.9
$(1/T)(10^3\ \mathrm{K})$	4.56	4.03	3.69	3.46	3.10	2.92
p/Torr	1	10	40	100	400	760
p/Pa	133.3	1333	5333	13332	53329	101325
$\ln(p/\mathrm{Pa})$	4.89	7.20	8.58	9.50	10.88	11.53

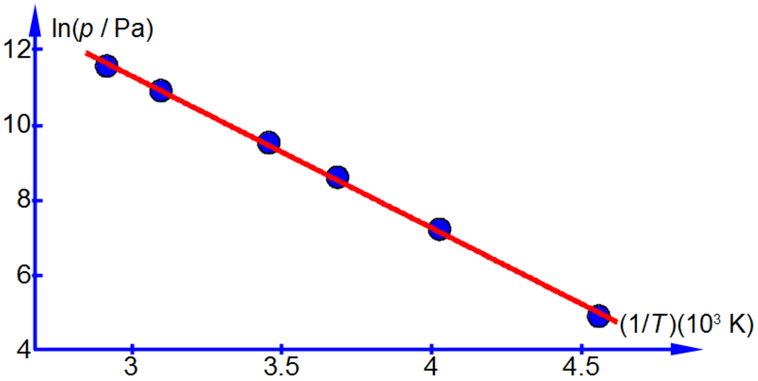


Figure 4.8: ln(p/Pa) versus (1/T)(10^3 K).

The straight line that I measured from the full sized manually drawn graph is $y = -4.044x + 23.43$ which taking into account the labels of the axes, including the unit multiples, gives the enthalpy of vaporization as

$$m = \frac{\ln(p/\mathrm{Pa})}{\left(\frac{1}{T}\right)(10^3\ \mathrm{K})} = -4.044 \qquad m = -4.044\times10^3\ \mathrm{K}$$

$$m = -\frac{\Delta H_{\mathrm{vap}}}{R} = \left(-4.044\times10^3\ \mathrm{K}\right)$$

$$\Delta H_{\mathrm{vap}} = \left(4.044\times10^3\ \mathrm{K}\right)\left(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\right) = 3.362\times10^4\ \mathrm{J\ mol^{-1}}$$

$$\Delta H_{\mathrm{vap}} = 33.62\ \mathrm{kJ\ mol^{-1}}$$

The student's measured value is higher by 16% than the accepted literature value of 28.85 kJ mol–1 and the method and apparatus both need careful evaluation.

Return to Question 5 (see page 77)

5 Week 5: Chemistry and Differentiation 1

5.1 Week 5 Tutorial Questions

5.1.1 Question 1: Molecules of a Gas

Consider an N_2 molecule at 298 K moving with a velocity of 515 m s^{-1}. In the absence of any collisions, how long will it take the molecule to travel 10 km? This *absence* of collisions corresponds to an extremely low pressure.

$$velocity = \frac{distance}{time} \qquad v = \frac{d}{t}$$

Jump to Solution 1 (see page 87)

5.1.2 Question 2: Molecules of a Gas

Remember that acceleration is the differential of the velocity-time curve (v-t graph) at a particular point in time.

$$acceleration = \frac{\mathrm{d}(velocity)}{\mathrm{d}(time)} \qquad a = \frac{\mathrm{d}\,v}{\mathrm{d}\,t}$$

Note that the symbol for differential is a roman (upright) "d" as it is not a variable but rather indicates an operation to be carried out on the variable, it is an "operator". The N_2 molecule collides with another molecule in a collision lasting 100 picoseconds (symbol ps and 1 ps = 10^{-12} s). As a result of the collision, the velocity of our N_2 molecule increases from 515 to 630 m s^{-1}. What is the acceleration of the molecule if it is still travelling in the same direction?

Jump to Solution 2 (see page 88)

5.1.3 Question 3: Molecules of a Gas

What force in newtons has been required to bring about the change in velocity of Question 2? Remember that

$$force = (mass)\times(acceleration) \qquad 1\ \mathrm{N} = 1\ \mathrm{kg\ m\ s^{-2}}$$

$$1\ \text{atomic mass unit, u} = 1.6605\times10^{-27}\ \mathrm{kg}$$

Jump to Solution 3 (see page 88)

5.1.4 Question 4: Molecules of a Gas

The N_2 molecule now travelling at 630 m s^{-1} has a collision with the walls of its containing vessel which again lasts for 100 ps. As a result of the wall collision the N_2 molecule is now travels at 630 m s^{-1} in the *opposite* direction. What has been its acceleration in this collision?

Jump to Solution 4 (see page 88)

5.1.5 Question 5: Maxwell-Boltzmann Distribution of Speeds of Gas Molecules

The fraction of identical molecules in a gas with speed c (ignoring the direction of the velocity) is $f(c)$ and is given by the Maxwell-Boltzmann distribution of speeds.

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

Where m is the molecular mass in kg; k is Boltzmann's constant which is the gas constant per molecule $k = R/T = 1.3807\times10^{-23}$ J K^{-1}; and T the temperature of the gas in K. Thus the Maxwell-Boltzmann distribution is *isotopic composition* dependent. We are now going to use a common trick which helps us see the wood from the trees. The first two terms are constant at a given temperature. So we can make the equation look less daunting by calling them a constant A. Secondly, we see that at a constant temperature the exponential term becomes $\exp(-Bc^2)$ where $B = m/2kT$. At constant temperature we have the equation.

$$f\left(c\right) = A\,c^2 \mathrm{e}^{-\left(Bc^2\right)}$$

Firstly, sketch the plot of the above $f(c)$ versus c equation. Secondly, by differentiating the equation with respect to c show that the graph has a maximum at $c_{\text{mp}} = (2kT/m)^{1/2}$ which can be identified with the most probable speed of a molecule, c_{mp}.

Jump to Solution 5 (see page 89)

5.1.6 Question 6: Measuring Rates of Reaction from Concentration Data

In a chemical reaction the concentration of a reagent [A] is found to decrease with time t as it is consumed to form products. A student measured the data below in the teaching lab.

$t/10^{-3}$ s	0.00	2.00	4.00	6.00	8.00	10.0
$\left[A\right]$/mol L^{-1}	1.00	0.605	0.366	0.221	0.134	0.081

The rate of a chemical reaction v is related to the differential change in concentration with time, in this reaction as below.

$$v = -\frac{\mathrm{d}\left[\mathrm{A}\right]}{\mathrm{d}\,t}$$

where the minus sign is to convert the negative slope (it is a *decrease* in reactant with time) into a positive rate of reaction. Firstly, draw a graph of [A] against time. Secondly, draw tangents to the graph and find values for the rate of reaction at times of $t = 0,\ 2.5\times10^{-3},\ 5.0\times10^{-3}$ and 7.5×10^{-3} s. What conclusion can you draw from these different rates of reaction as a function of time?

Jump to Solution 6 (see page 91)

5.2 Week 5 Tutorial Solutions

5.2.1 Solution 1: Molecules of a Gas

$$v = \frac{d}{t} \qquad t = \frac{d}{v} = \frac{10000\ \mathrm{m}}{515\ \mathrm{m\ s^{-1}}}$$

$$t = 19.4\ \mathrm{s}$$

Notice how in the *absence* of any collision a molecules can travel a long distance very quickly, *e.g.* inside a mass spectrometer flight-tube where the pressure may be 10^{-9} atmospheres or less, or in space. Of course, at any ambient pressures the molecules are rapidly colliding with one another and changing their directions as well as their speeds but nevertheless the *average* speed of N_2 at room temperature is still around 515 m s^{-1}.

Return to Question 1 (see page 85)

5.2.2 Solution 2: Molecules of a Gas

Acceleration, a, is the gradient of the velocity-time graph (v-t graph) which in this case is

$$a = \frac{\mathrm{d}v}{\mathrm{d}t} \qquad a = \frac{630\ \mathrm{m\ s^{-1}} - 515\ \mathrm{m\ s^{-1}}}{100 \times 10^{-12}\ \mathrm{s}}$$

$$\boxed{a = 1.15 \times 10^{12}\ \mathrm{m\ s^{-2}}}$$

Notice how molecules are capable of very rapid acceleration (also deceleration) by means of collisions.

Return to Question 2 (see page 85)

5.2.3 Solution 3: Molecules of a Gas

N_2 has a mass of 28 u where the atomic mass unit $u = 1.6605 \times 10^{-27}$ kg.

$$F = m \times a \qquad F = \left(28 \times 1.6605 \times 10^{-27}\ \mathrm{kg}\right)\left(1.15 \times 10^{12}\ \mathrm{m\ s^{-2}}\right)$$

$$\boxed{F = 5.35 \times 10^{-14}\ \mathrm{kg\ m\ s^{-2}}}$$

The named unit for force is the newton (lower case “n” for the unit and upper case for the person) and its symbol is N (upper case) where

$$\boxed{1\ \mathrm{N} = 1\ \mathrm{kg\ m\ s^{-2}} \qquad F = 5.35 \times 10^{-14}\ \mathrm{N}}$$

Return to Question 3 (see page 85)

5.2.4 Solution 4: Molecules of a Gas

$$a = \frac{\left(630\ \mathrm{m\ s^{-1}}\right) - \left(-630\ \mathrm{m\ s^{-1}}\right)}{100 \times 10^{-12}\ \mathrm{s}} = \frac{1260\ \mathrm{m\ s^{-1}}}{1.00 \times 10^{-10}\ \mathrm{s}}$$

$$\boxed{a = 1.26 \times 10^{13}\ \mathrm{m\ s^{-2}}}$$

As well as molecule-molecule collisions, collisions with the vessel walls also cause molecules to undergo very rapid acceleration or deceleration.

Return to Question 4 (see page 86)

5.2.5 Solution 5: Maxwell-Boltzmann Distribution of Speeds of Gas Molecules

$$f(c) = Ac^2 e^{-(Bc^2)}$$

We see that the equation is the product of two terms in c, The first, c^2, makes $f(c)$ increase from zero upwards with increasing c. The negative exponential term makes $f(c)$ *decrease* from 1.0 downwards towards zero with increasing c. So the fraction $f(c)$, the product of these two terms, will start from zero for $c = 0$, then drop back to zero at large values of c and for intermediate values of c the fraction will pass through a maximum value. Fig. 5.1 shows the two constituent curves in red and the product of them in blue.

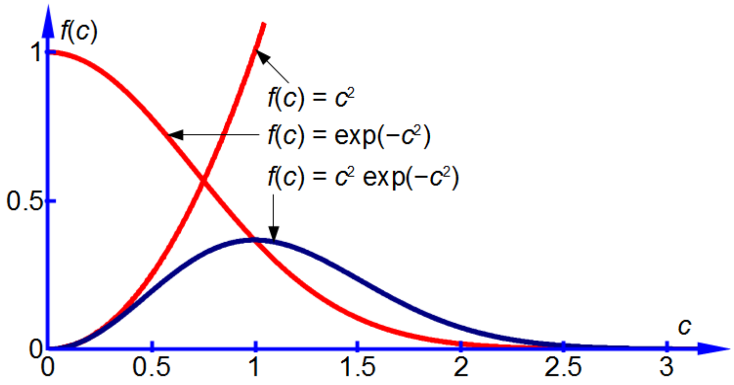


Figure 5.1: $f(c)$ versus c for $f(c) = c^2$, $f(c) = \exp(-c^2)$ and $f(c) = c^2 \exp(-c^2)$.

The maximum is when $df(c)/dc = 0$ and we need to differentiate the equation. Let $y = Ac^2$ and $x = \exp(-Bc^2)$ so that $f(c) = x \times y$ and use the rule for the differentiation of a product of two functions.

$$\frac{d f(c)}{d c} = x \frac{d y}{d c} + y \frac{d x}{d c}$$

$$y = Ac^2 \qquad \frac{d y}{d c} = 2Ac$$

$$x = e^{-(Bc^2)} \qquad \frac{dx}{dc} = (-2Bc)e^{-(Bc^2)}$$

$\mathrm{d}x/\mathrm{d}c$ has come from using the general form of the differential of an exponential power term

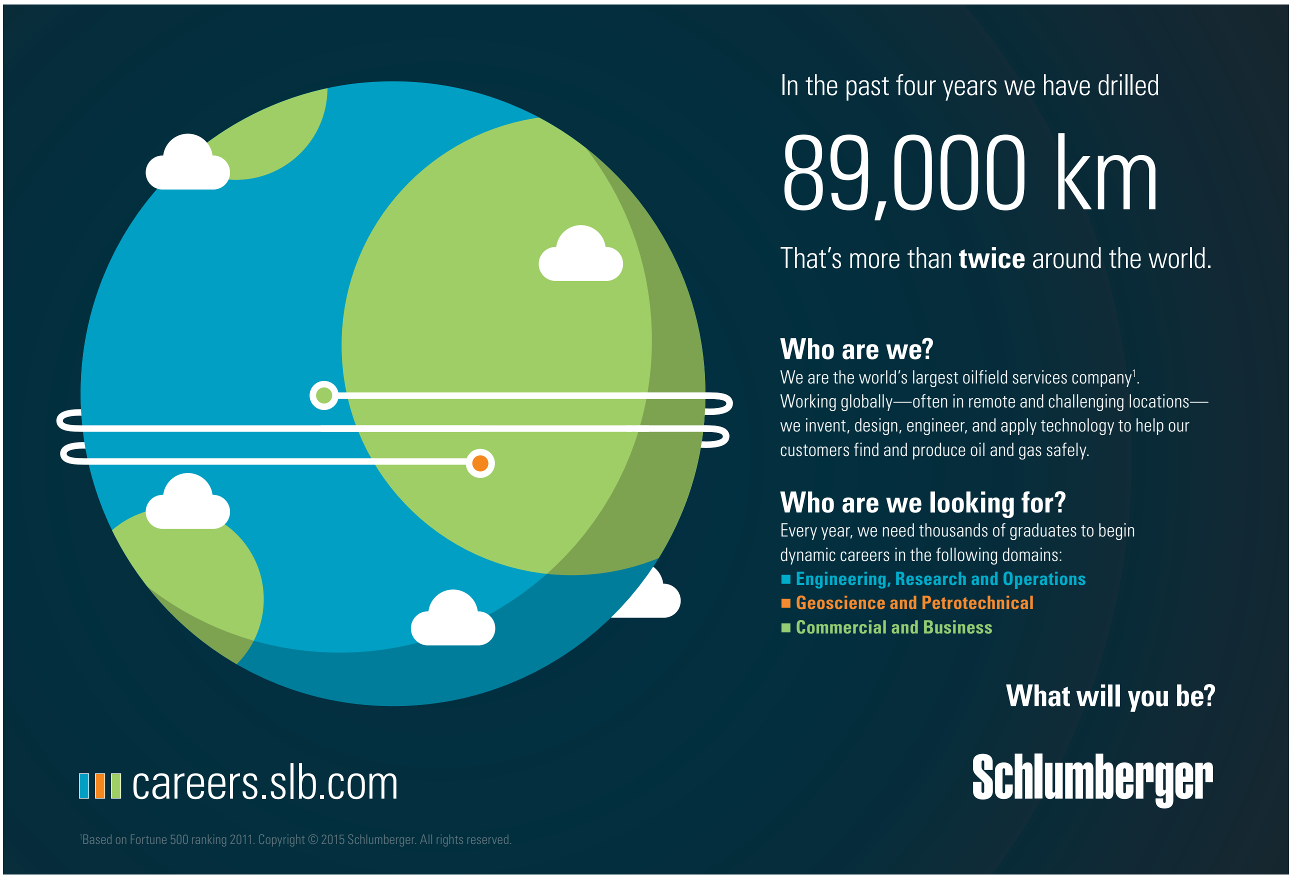
$$\frac{\mathrm{d}\,\mathrm{e}^{u}}{\mathrm{d}\,x} = \frac{\mathrm{d}\,u}{\mathrm{d}\,x}\mathrm{e}^{u}$$

Therefore from the differentiation of a product of two functions we have the following

$$\frac{\mathrm{d}\,f(c)}{\mathrm{d}\,c} = \mathrm{e}^{-(B\,c^{2})}(2\,A\,c) + (A\,c^{2})(-2\,B\,c)\,\mathrm{e}^{-(B\,c^{2})}$$

Therefore when $\mathrm{d}f(c)/\mathrm{d}c = 0$ we can find the maximum in $f(c)$ which gives the molecular speed at the maximum *i.e.* the most probable speed *c*mp

$$\mathrm{e}^{-(B\,c_{\mathrm{mp}}^{2})}(2\,A\,c_{\mathrm{mp}}) = (A\,c_{\mathrm{mp}}^{2})(2\,B\,c_{\mathrm{mp}})\,\mathrm{e}^{-(B\,c_{\mathrm{mp}}^{2})}$$



Cancelling out terms.

$$1 = B c_{\text{mp}}^2 \qquad c_{\text{mp}} = \sqrt{\frac{1}{B}}$$

$$\boxed{c_{\text{mp}} = \sqrt{\frac{2kT}{m}}}$$

Return to Question 5 (see page 86)

5.2.6 Solution 6: Measuring Rates of Reaction from Concentration Data

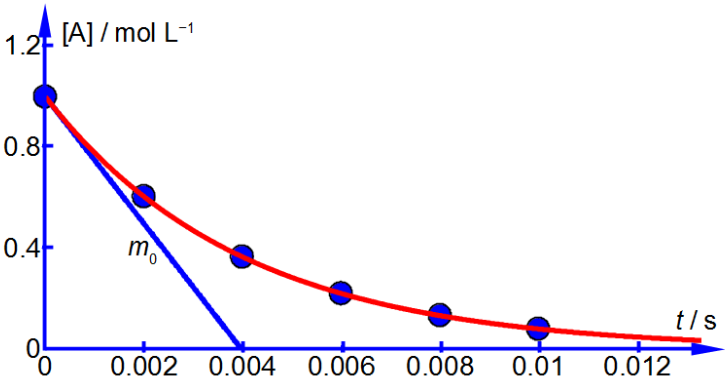


Figure 5.2: concentration of [A] versus time, showing the gradient at $t = 0$ s.

Fig. 5.2 shows the reagent concentration against time graph and *one* of the gradients drawn at zero time which is $m_0 = -251$ mol L^{-1} s^{-1}. As the rate of a chemical reaction is defined as always positive this gives the rate, v, at $t = 0$ as $v_0 = 251$ mol L^{-1} s^{-1}. Drawing similar gradients to the smooth curve gives the followings rates.

$t/10^{-3}$ s	0	2.5	5.0	7.5
v/mol L^{-1} s^{-1}	251	134	71.5	38.2

The data shows that the rate of reaction, v, decreases with time because the concentration of reactant [A] is decreasing as it is consumed forming the product.

Return to Question 6 (see page 86)

6 Week 6: Chemistry and Differentiation 2

6.1 Week 6 Tutorial Questions

6.1.1 Question 1: Intermolecular Interactions

The non-bonding interaction between two neutral atoms or two neutral molecules, their intermolecular interaction, is given by the Lennard-Jones equation.

$$V = -4\,\varepsilon\left(\left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r}\right)^{12}\right)$$

Where V is the potential energy of the interacting molecules, r is the distance between the two molecules and ε is the depth of the potential well. The 6th-power term describes the long-range *attraction* between the molecules due to the van der Waals or dispersion forces. The 12th-power term represents the short-range *repulsion* between the molecules from the overlap of their electron orbitals when the distance between the molecules becomes so small that they are essentially in contact. For the interaction between two N_2 molecules the constants are $\varepsilon = 765\ \mathrm{J\ mol^{-1}}$ and $\sigma = 3.92\times10^{-10}\ \mathrm{m}$. Sketch the shape of the graph for this potential.

Jump to Solution 1 (see page 95)

6.1.2 Question 2: Intermolecular Interactions

$$V = -4\,\varepsilon\left(\left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r}\right)^{12}\right)$$

The variables in the Lennard-Jones equation are V and r, Firstly, find the derivatives of V with respect to r $\mathrm{d}V/\mathrm{d}r$. Secondly, differentiate the first derivative with respect to r to find the second derivative $\mathrm{d}^2V/\mathrm{d}r^2$ for the interaction between N_2 molecules.

Jump to Solution 2 (see page 97)

6.1.3 Question 3: Intermolecular Interactions

Use the solutions of Question 2 to find the separation at which the Lennard-Jones potential V is at a minimum, that is the distance between two N_2 molecules at which the potential energy is a minimum.

Jump to Solution 3 (see page 97)

6.1.4 Question 4: Changes in pH

The pH of a solution in which the hydrogen ion concentration is $[\mathrm{H}^+]$ is defined by:

$$\mathrm{pH} = -\log\left[\mathrm{H}^+\right]$$

Firstly, show that $d(\mathrm{pH})/d[\mathrm{H}^+]$ arising from a small change in pH of $d(\mathrm{pH})$ resulting from a small change in $[\mathrm{H}^+]$ of $d[\mathrm{H}^+]$ is proportional to the ratio $d[\mathrm{H}^+]/[\mathrm{H}^+]$. Secondly, a solution originally with $[\mathrm{H}^+] = 0.02\ \mathrm{mol\ L^{-1}}$ had an additional concentration of $d[\mathrm{H}^+] = 5\times10^{-4}\ \mathrm{mol\ L^{-1}}$ added to it, calculate the change in pH, $d(\mathrm{pH})$.

Jump to Solution 4 (see page 98)

6.1.5 Question 5: Differentiation of the Arrhenius Equation

The rate constant k for a chemical reaction is related to the temperature T by the Arrhenius equation.

$$k = A\mathrm{e}^{-\left(\frac{E_\mathrm{a}}{RT}\right)}$$

Where A and E_a are constants for a given chemical reaction; R is the gas constant $R = 8.314$ J K^{-1} mol^{-1}; and T is the absolute temperature in K. For a particular biochemical reaction $k = 20$ L mol^{-1} s^{-1} when $T = 300$ K. If $E_a = 50$ kJ mol^{-1} for this reaction, by differentiating the Arrhenius equation with respect to T, find the change in the value of k when T increases by 1 K to 301 K. Remember to use the base unit of $E_a = 50000$ J mol^{-1} in the calculation and not its multiple of kJ mol^{-1}.

Jump to Solution 5 (see page 99)

6.1.6 Question 6: Consecutive Chemical Reactions

Two chemical reactions consecutively follow on from one another. Consecutive reactions are generally very common in biochemistry and organic chemistry.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

A common situation is for k_1 to be a *first-order* rate constant at which A is transformed to B and k_2 the *first-order* rate constant at which B transformed to product C. Assuming that we start at time zero with pure A and no B or C present then this mechanism gives the concentration of B, [B], at any later time, t, as

$$[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right)$$

where $[\mathrm{A}]_0$ is the initial concentration of A. Find the time, in terms of the rate constants k_1 and k_2, at which the concentration of B is a maximum $[\mathrm{B}]_{\mathrm{max}}$.

Jump to Solution 6 (see page 100)

6.1.7 Question 7: Consecutive Chemical Reactions

$$[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right)$$

Firstly, construct a table of data of [B], t and d[B]/dt. The table should run from time $t = 0$ to $t = 1$ s in intervals of 0.1 s. Secondly, assuming that $[\mathrm{A}]_0 = 1$ mol L^{-1} and that the rate constants are $k_1 = 7.0$ s^{-1} and $k_2 = 5.0$ s^{-1}, draw a graph of [B] versus t and a graph of d[B]/dt versus t. Thirdly. find the time, t_{max}, at which the concentration of [B] is at a maximum on your graph and check that this is consistent with your solution of Question 6. Fourthly, find the value of $[\mathrm{B}]_{\mathrm{max}}$.

Jump to Solution 7 (see page 101)

6.1.8 Question 8: Consecutive Chemical Reactions: the Steady State Approximation

$$[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right)$$

By consideration of each of the terms in the equation show that if k_2 is very much larger than k_1 *i.e.* $k_2 \gg k_1$ then [B] and d[B]/dt will be both small and approximately constant.

Jump to Solution 8 (see page 103)

6.1.9 Question 9: Consecutive Chemical Reactions with a Rate Determining Step

$$[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right)$$

By consideration of each of the terms of the equation find approximate expressions for [B] and d[B]/dt when k_1 is very much larger than k_2 *i.e.* $k_1 \gg k_2$.

Jump to Solution 9 (see page 104)

6.2 Week 6 Tutorial Solutions

6.2.1 Solution 1: Intermolecular Interactions

$$V = -4\,\varepsilon\left(\left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r}\right)^{12}\right)$$

To sketch the above equation we can simplify it to $V = -Ar^{-6} + Br^{-12}$ and separately plot the shape of r^{-6} and r^{-12} and then "add" their shapes to arrive at the final shape of the graph as shown in Fig. 6.1. The position of the minimum and its depth depend upon the values of A and B (that is upon the values of ε and σ). The $-Ar^{-6}$ term being negative decreases the potential as the molecules get closer, they are attracting one another due to the van der Waals forces. The power of –6 in $-Ar^{-6}$ acts at longer range than the $+Br^{-12}$ term. The $+Br^{-12}$ term is effective at short range and increases the potential as the distance decreases and the molecules increasingly repel one another.

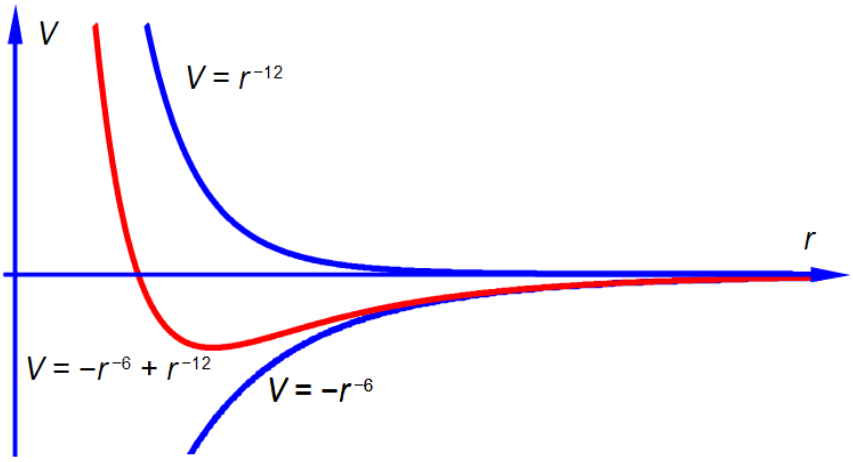
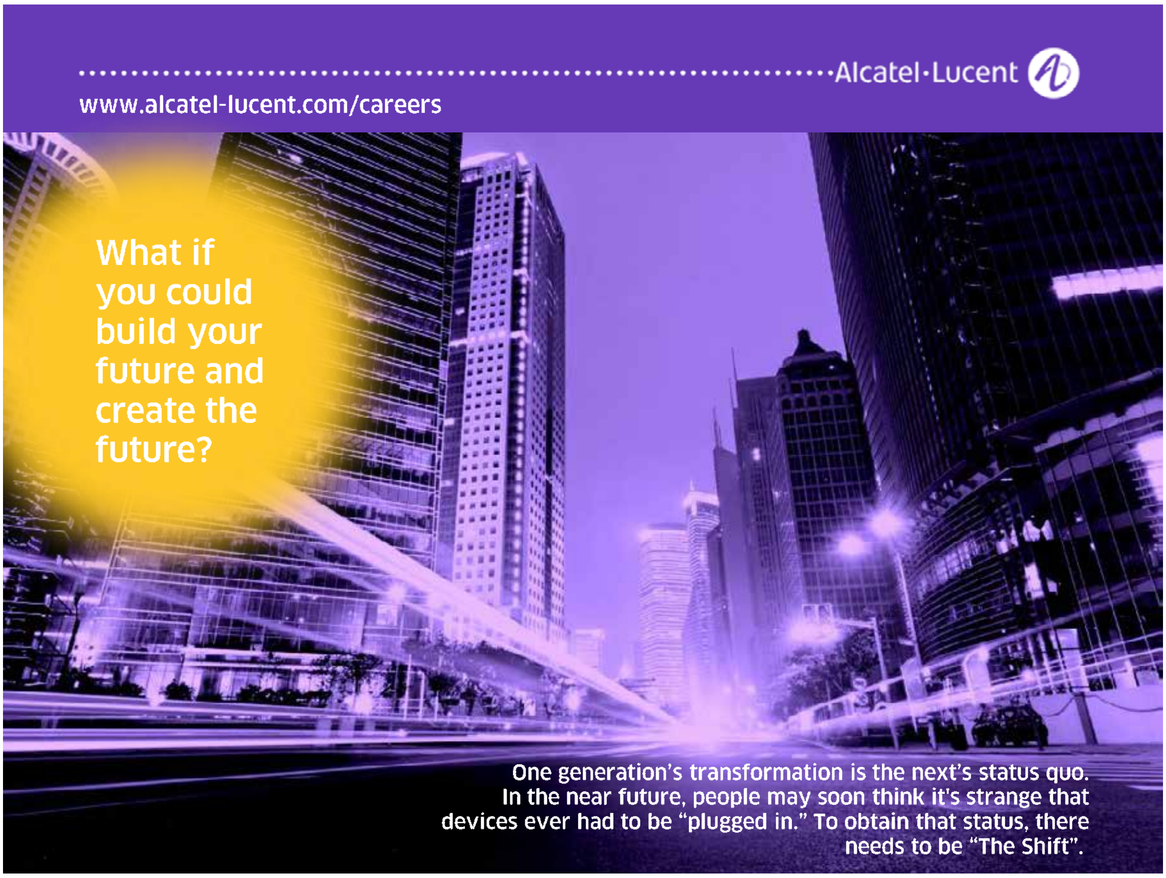


Figure 6.1: sketch of $V = -r^{-6}$, $V = +r^{-12}$, and the combined plot of $V = -r^{-6} + r^{-12}$.

Return to Question 1 (see page 92)



6.2.2 Solution 2: Intermolecular Interactions

Bring the denominators of the pair of inner brackets up to the numerators before differentiating.

$$V = -4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r}\right)^{12}\right) \qquad V = -4\varepsilon\left(\sigma^{6} r^{-6} - \sigma^{12} r^{-12}\right)$$

$$\frac{\mathrm{d}V}{\mathrm{d}r} = -4\varepsilon\left(-6\sigma^{6} r^{-7} - (-12)\sigma^{12} r^{-13}\right)$$

$$\boxed{\frac{\mathrm{d}V}{\mathrm{d}r} = -4\varepsilon\left(-\frac{6\sigma^{6}}{r^{7}} + \frac{12\sigma^{12}}{r^{13}}\right)}$$

$$\frac{\mathrm{d}^2 V}{\mathrm{d}r^2} = -4\varepsilon\left((-6)(-7)\sigma^{6} r^{-8} + (12)(-13)\sigma^{12} r^{-14}\right)$$

$$\boxed{\frac{\mathrm{d}^2 V}{\mathrm{d}r^2} = -4\varepsilon\left(\frac{42\sigma^{6}}{r^{8}} - \frac{156\sigma^{12}}{r^{14}}\right)}$$

Return to Question 2 (see page 92)

6.2.3 Solution 3: Intermolecular Interactions

To find the separation at which the potential V is at a minimum we use the first derivative. Leaving σ in angstroms will give r in angstroms. For clarity I have not shown the units in this evaluations of the equation.

$$\frac{\mathrm{d}V}{\mathrm{d}r} = -4\varepsilon\left(-\frac{6\sigma^{6}}{r^{7}} + \frac{12\sigma^{12}}{r^{13}}\right)$$

Either 4ε must equal zero, which it cannot, or the term in brackets equals zero giving the following,

$$\frac{6(3.92)^{6}}{r_{\min}^{7}} = \frac{12(3.92)^{12}}{r_{\min}^{13}} \qquad \frac{r_{\min}^{13}}{r_{\min}^{7}} = \frac{12(3.92)^{12}}{6(3.92)^{6}} \qquad r_{\min}^{6} = 2\times 3.92^{6}$$

$$\boxed{r_{\min} = 4.40\ \text{Å}}$$

$r_{\min} = 4.40\ \text{Å}$ is the separation of *two* N_2 molecules at the minimum potential energy (see Fig. 6.2) and is larger than the 3.7 Å "hard sphere" molecular diameter of N_2.

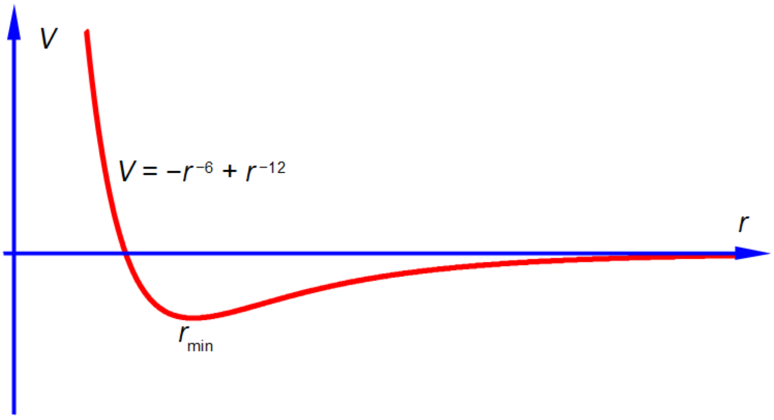


Figure 6.2: Lennard-Jones plot with the intermolecular distance r_{min} at the minimum potential.

Return to Question 3 (see page 92)

6.2.4 Solution 4: Changes in pH

$$\text{pH} = -\log\left[\text{H}^+\right]$$

As we need to differentiate this, we first need to convert it to natural logarithms. From section 3.1 and letting $x = [\text{H}^+]$ we have

$$\log_b(a) \times \log_a(x) = \log_b(x)$$

$$\log_e(10) \times \log_{10}\left[\text{H}^+\right] = \log_e\left[\text{H}^+\right] \qquad \ln(10) \times \log_{10}\left[\text{H}^+\right] = \ln\left[\text{H}^+\right]$$

$$2.303 \log_{10}\left[\text{H}^+\right] = \ln\left[\text{H}^+\right] \qquad \log_{10}\left[\text{H}^+\right] = \frac{1}{2.303}\ln\left[\text{H}^+\right] \qquad \text{pH} = -\frac{1}{2.303}\ln\left[\text{H}^+\right]$$

Note the negative sign, we may now differentiate the above equation, then treat the differential as separable terms and then substitute the values for the variables.

$$\frac{\text{d}(\text{pH})}{\text{d}\left[\text{H}^+\right]} = -\frac{1}{2.303}\frac{1}{\left[\text{H}^+\right]} \qquad \text{d}(\text{pH}) = -\frac{1}{2.303}\frac{\text{d}\left[\text{H}^+\right]}{\left[\text{H}^+\right]}$$

$$\text{d}(\text{pH}) = -\frac{1}{2.303}\frac{5 \times 10^{-4}\ \text{mol L}^{-1}}{0.02\ \text{mol L}^{-1}}$$

$$\text{d}(\text{pH}) = -0.011$$

As expected *increasing* the hydrogen ion concentration leads to a *decrease* in pH.

Return to Question 4 (see page 93)

6.2.5 Solution 5: Differentiation of the Arrhenius Equation

$$k = A\mathrm{e}^{-\left(\frac{E_\mathrm{a}}{RT}\right)} \qquad \left(20\ \mathrm{L\ mol^{-1}\ s^{-1}}\right) = A\mathrm{e}^{-\frac{50000\ \mathrm{J\ mol^{-1}}}{\left(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)\left(300\ \mathrm{K}\right)}}$$

$$\boxed{A = 1.017\times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}}}$$

Let $x = 1/T$ then $\mathrm{d}x/\mathrm{d}T = -T^{-2}$ and so,

$$k = A\mathrm{e}^{-\left(\frac{E_\mathrm{a}}{R}x\right)} \qquad \frac{\mathrm{d}k}{\mathrm{d}x} = A\left(-\frac{E_\mathrm{a}}{R}\right)\mathrm{e}^{-\left(\frac{E_\mathrm{a}}{R}x\right)} \qquad \frac{\mathrm{d}k}{\mathrm{d}x} = A\left(-\frac{E_\mathrm{a}}{R}\right)\mathrm{e}^{-\left(\frac{E_\mathrm{a}}{RT}\right)}$$

$$\frac{\mathrm{d}k}{\mathrm{d}T} = \frac{\mathrm{d}x}{\mathrm{d}T}\times\frac{\mathrm{d}k}{\mathrm{d}x} \qquad \frac{\mathrm{d}k}{\mathrm{d}T} = \left(-\frac{1}{T^2}\right)\times A\left(-\frac{E_\mathrm{a}}{R}\right)\mathrm{e}^{-\left(\frac{E_\mathrm{a}}{RT}\right)}$$

$$\boxed{\frac{\mathrm{d}k}{\mathrm{d}T} = \frac{AE_\mathrm{a}}{RT^2}\mathrm{e}^{-\left(\frac{E_\mathrm{a}}{RT}\right)}}$$

Treating the differential as separable terms and substituting the values for the variables with $\mathrm{d}T = 1$ K gives

$$\mathrm{d}k = \mathrm{d}T \frac{AE_\mathrm{a}}{RT^2} \mathrm{e}^{-\left(\frac{E_\mathrm{a}}{RT}\right)}$$

$$\mathrm{d}k = (1\ \mathrm{K}) \frac{(1.017\times10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}})(50000\ \mathrm{J\ mol^{-1}})}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\ \mathrm{K})^2} \mathrm{e}^{-\left(\frac{50000\ \mathrm{J\ mol^{-1}}}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\ \mathrm{K})}\right)}$$

$$\mathrm{d}k = 1.337\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

Return to Question 5 (see page 93)

6.2.6 Solution 6: Consecutive Chemical Reactions

$$[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right)$$

To find the maximum concentration of B we differentiate [B] with respect to *t*. Notice that on the right hand side the terms before the bracket are constant and differentiating with respect to *t*, gives

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(-k_1 \mathrm{e}^{-k_1 t} + k_2 \mathrm{e}^{-k_2 t}\right)$$

The maximum in [B] occurs when $\mathrm{d}[\mathrm{B}]/\mathrm{d}t = 0$, which is either when $[\mathrm{A}]_0 k_1/(k_2 - k_1)$ is equal to zero (which it cannot be) or alternatively the term is brackets equals zero.

$$k_1 \mathrm{e}^{-k_1 t} = k_2 \mathrm{e}^{-k_2 t}$$

Taking natural logs allows us to find *t* at which [B] is a maximum.

$$\ln(k_1) - k_1 t = \ln(k_2) - k_2 t \qquad \ln(k_1) - \ln(k_2) = t(k_1 - k_2) \qquad \ln\left(\frac{k_1}{k_2}\right) = t(k_1 - k_2)$$

$$t = \frac{1}{k_1 - k_2}\ln\left(\frac{k_1}{k_2}\right)$$

The time at which the concentration of B is a maximum depends only on the values of the two rate constants and is independent of the initial concentration of A.

Return to Question 6 (see page 94)

6.2.7 Solution 7: Consecutive Chemical Reactions

From Solution 6 we have d[B]/d*t*

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=[\mathrm{A}]_0\frac{k_1}{k_2-k_1}\left(-k_1\mathrm{e}^{-k_1 t}+k_2\mathrm{e}^{-k_2 t}\right)$$

and substituting in the values for the variables gives Table 6.1 which are plotted in Fig. 6.3 and Fig. 6.4.

t/s	$[\mathrm{B}]/\mathrm{mol\ L^{-1}}$	$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}/\mathrm{mol\ L^{-1}\ s^{-1}}$
0.0	0.000	7.000
0.1	0.385	1.552
0.2	0.424	−0.396
0.3	0.352	−0.905
0.4	0.261	−0.879
0.5	0.182	−0.697
0.6	0.122	−0.504
0.7	0.080	−0.346
0.8	0.051	−0.230
0.9	0.032	−0.149
1.0	0.020	−0.096

Table 6.1: *t*, [B], and d[B]/d*t*.

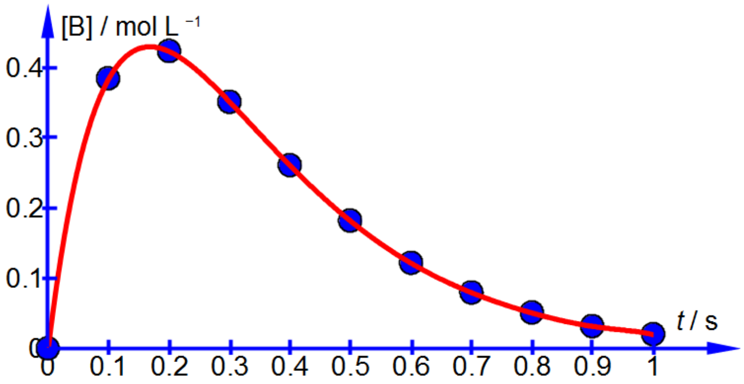


Figure 6.3: [B]/mol L^{-1} versus *t*/s.

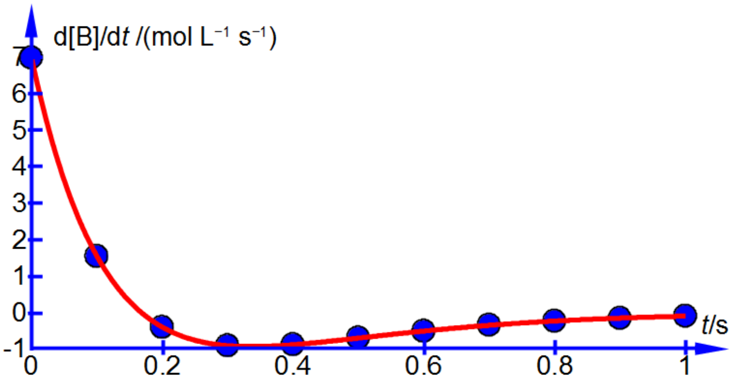


Figure 6.4: d[B]/d*t* /(mol L^{-1} s^{-1}) versus *t*/s.

From Solution 6 we have the equation for the time at which d[B]/d*t* is zero *i.e.* the time at which [B] is a maximum and substituting the values (but not the units for clarity) gives the time at maximum [B] as

$$t = \frac{1}{k_1 - k_2}\ln\left(\frac{k_1}{k_2}\right) = \frac{1}{7-5}\ln\left(\frac{7}{5}\right)$$

$$t = 0.168\ \text{s}$$

Substituting this time (t = 0.168 s) along with $[\mathrm{A}]_0 = 1$ mol L^{-1}, $k_1 = 7.0$ s^{-1}, $k_2 = 5.0$ s^{-1}, into the expression for [B] gives $[\mathrm{B}]_{\max}$.

$$[\mathrm{B}]_{\max} = \left(1\ \mathrm{mol\ L^{-1}}\right)\frac{\left(7.0\ \mathrm{s^{-1}}\right)}{\left(5.0\ \mathrm{s^{-1}}\right)-\left(7.0\ \mathrm{s^{-1}}\right)}\left(\mathrm{e}^{-\left(7.0\ \mathrm{s^{-1}}\right)\left(0.168\ \mathrm{s}\right)}-\mathrm{e}^{-\left(5.0\ \mathrm{s^{-1}}\right)\left(0.168\ \mathrm{s}\right)}\right)$$

$$[\mathrm{B}]_{\max} = \left(-3.5\ \mathrm{mol\ L^{-1}}\right)\left(\mathrm{e}^{-\left(7.0\ \mathrm{s^{-1}}\right)\left(0.168\ \mathrm{s}\right)}-\mathrm{e}^{-\left(5.0\ \mathrm{s^{-1}}\right)\left(0.168\ \mathrm{s}\right)}\right)$$

$$\boxed{[\mathrm{B}]_{\max} = 0.431\ \mathrm{mol\ L^{-1}}}$$

The value of $[\mathrm{B}]_{\max} = 0.431$ mol L^{-1} from the differentiation of the rate equation agrees with the graphical value in Fig. 6.3.

Return to Question 7 (see page 94)

6.2.8 Solution 8: Consecutive Chemical Reactions: the Steady State Approximation

$$[\mathrm{B}] = [\mathrm{A}]_0\frac{k_1}{k_2-k_1}\left(\mathrm{e}^{-k_1t}-\mathrm{e}^{-k_2t}\right)$$

When $k_2 \gg k_1$ then the following approximations may be made. From Fig. 6.5 we have as k_2 is dominantly large then $\exp(-k_2t) \approx 0$ and as k_1 is small and *positive* then $\exp(-k_1t) \approx \exp(0) \approx 1$. Finally $(k_2 - k_1) \approx k_2$.

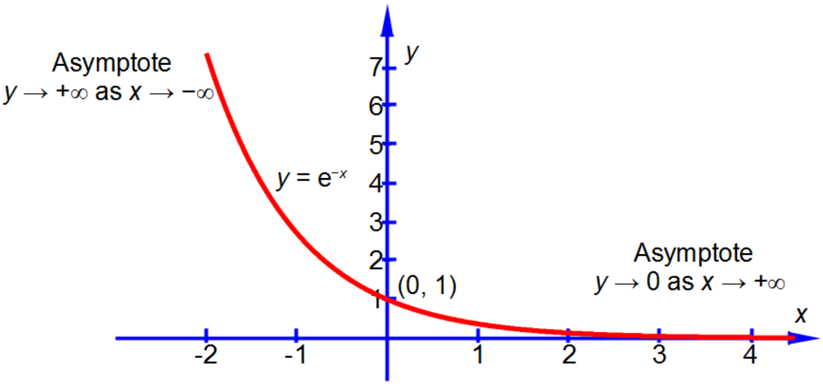


Figure 6.5: shape of a negative exponential, → means "tends to".

$$[\mathrm{B}] = [\mathrm{A}]_0\frac{k_1}{k_2-k_1}\left(\mathrm{e}^{-k_1t}-\mathrm{e}^{-k_2t}\right) \approx [\mathrm{A}]_0\frac{k_1}{k_2}\left(1-0\right)$$

$$\boxed{[\mathrm{B}] \approx [\mathrm{A}]_0\frac{k_1}{k_2}}$$

As k_1/k_2 is a small number thus [B] will be small compared to $[A]_0$. Using the same approximations as above with the equation for the rate of forming the intermediate d[B]/dt we have

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(-k_1 \mathrm{e}^{-k_1 t} + k_2 \mathrm{e}^{-k_2 t}\right) \approx [\mathrm{A}]_0 \frac{k_1}{k_2}\left(\left(-k_1 \times 1\right) + \left(k_2 \times 0\right)\right)$$

$$\boxed{\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} \approx -[\mathrm{A}]_0 \frac{k_1^{\,2}}{k_2}}$$

As k_1/k_2 is a small number then k_1^2/k_2 is an *even smaller* number and thus the rate of change of the [B] concentration is exceedingly small, *i.e.* [B] is approximately constant. Thus the intermediate concentration [B] is *both small and approximately constant* under the approximations which follow from where $k_2 \gg k_1$ and this is called the "Steady State Approximation" in chemical kinetics, see Fig. 6.6.

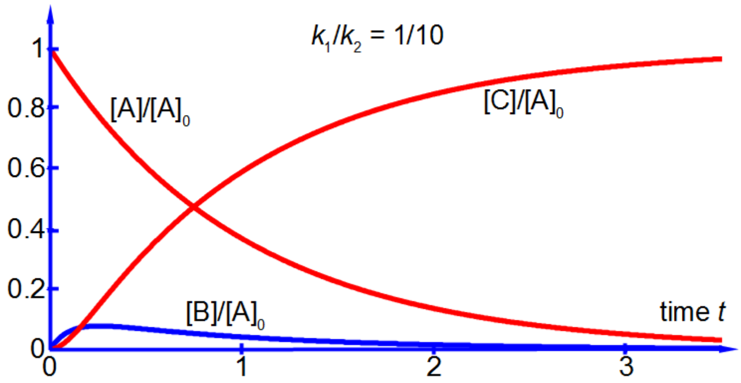


Figure 6.6: relative concentrations versus time for k_1/k_2 = 1/10.

The steady state approximation does *not* assume the reaction intermediate concentration to be constant and therefore its time derivative being zero. The steady state approximation *assumes* that the *variation* in the concentration of the intermediate is *approximately* zero and as the concentration of the intermediate is so low that even a large relative variation in its concentration is small if compared quantitatively against those of the reactant and product.

Return to Question 8 (see page 95)

6.2.9 Solution 9: Consecutive Chemical Reactions with a Rate Determining Step

$$[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right)$$

When $k_1 \gg k_2$ (the opposite conditions from Solution 8) then the following approximations may be made from Fig. 6.5 for negative exponential functions. The condition ($k_1 \gg k_2$) means k_1 is much larger than k_2 and thus $\exp(-k_1 t) \approx 0$ and as k_2 is small and *positive* then $\exp(-k_2 t) \approx \exp(0) \approx 1$ and $(k_2 - k_1) \approx -k_1$.

$$[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right) \approx [\mathrm{A}]_0 \frac{k_1}{-k_1}(0-1) \approx [\mathrm{A}]_0$$

As $[\mathrm{B}] \approx [\mathrm{A}]_0$ over part of reaction time, see Fig. 6.7, the final product concentration [C] does not start to increase appreciably until the intermediate concentration [B] has passed its maximum by which time the reactant concentration [A] in negligible. Using the same *approximations* as above with the equation for the rate of forming the intermediate d[B]/d*t* we have

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(-k_1 \mathrm{e}^{-k_1 t} + k_2 \mathrm{e}^{-k_2 t}\right) \approx [\mathrm{A}]_0 \frac{k_1}{-k_1}\left(\left(-k_1 \times 0\right) + \left(k_2 \times 1\right)\right)$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} \approx -[\mathrm{A}]_0 k_2$$

Over much of the reaction the rate of change of the intermediate concentration d[B]/d*t* to form the product C will approximately depend on the rate of the slow "Rate Determining Step" k_2.

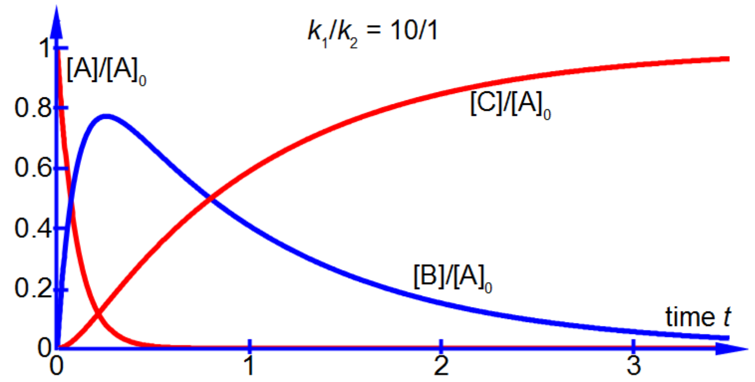


Figure 6.7: relative concentrations versus time for $k_1/k_2 = 10/1$.

Return to Question 9 (see page 95)

7 Week 7: Chemistry and Integration 1

This introduction to integration is spread over both weeks 7 and 8. The tutorials questions and solutions will show some of the more important Chemical applications of the Maths technique of integration. One very common Maths technique used in Chemistry is the “separation of variables” method for integrating a differential equation. This is covered in the solutions for this week (Section 7.2).

7.1 Week 7 Tutorial Questions

7.1.1 Question 1: Radioactive Decay

The decay of a radioactive element $A \rightarrow P$ has a rate constant k. Radioactive decay is a first-order chemical reaction with $[A]$ and t being the variables of the equation.

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

The rate of reaction is equal to rate of loss of [A] with time t which is equal to the product of the rate constant k and the concentration [A]. The negative sign is to give a *positive* rate constant for a reaction which involves the *loss* of the *reactant*. In order to obtain an equation which will give us the concentration of A at any time we need to integrate this equation from $t = 0$ when $[A] = [A]_0$ to a general time $t = t$ when $[A] = [A]_t$. Carry out this definite integration for this first-order chemical reaction.

Jump to Solution 1 (see page 109)

7.1.2 Question 2: Second-Order Chemical Reactions

If the overall (or stoichiometric) reaction is two molecules of A reacting to give products $2A \rightarrow P$ with rate constant k then for *some* mechanisms we *may* have a second-order reaction. An example of such a second-order reaction is that of nitrogen dioxide

$$2\,NO_2 \longrightarrow 2\,NO + O_2$$

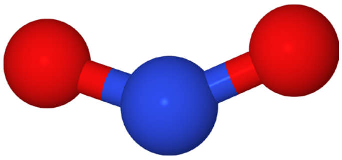


Figure 7.1: nitrogen dioxide molecule, N = blue, O = red.

NO_2 is involved in important chemical reactions in polluted atmospheres and also in the industrial manufacture of nitric acid. Using the general symbol [A] rather than the specific one $[NO_2]$ we find the rate of loss of A is expressed by the second-order kinetics equation below.

$$\frac{d[A]}{dt} = -k[A]^2$$

In order to obtain an equation which will give us the concentration of A at any time we need to integrate this equation from $t = 0$ when $[A] = [A]_0$ to a general time $t = t$ when $[A] = [A]_t$. Carry out this definite integration for this second-order chemical reaction.

Jump to Solution 2 (see page 110)

7.1.3 Question 3: Expanding Gas and Thermodynamic Work

In Chemistry it is very common to have gases being formed, reacting, compressed or expanding. A simple way of understanding such processes is to begin with a "mechanical" picture of a gas trapped inside a cylinder by a piston, Fig. 7.2.

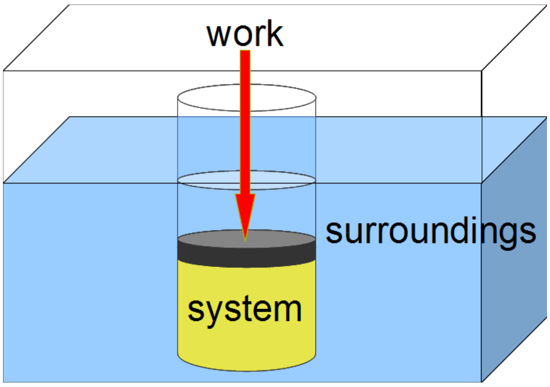


Figure 7.2: thermodynamic definitions.

The gas is called “the system” in thermodynamics and everything other than the gas is called “the surroundings”. If the pressure of the system p is the same as the surroundings and the volume of the system is V then the work done *on the system* (gas) is given the symbol w. As the gas expands at constant temperature, T, the work done *on* the system (the gas) is shown in the equation below.

$$w = -\int p \, \mathrm{d}V$$

The negative sign arises because as the system expands then $\mathrm{d}V > 0$ and the gas does work on the surroundings, pushing the surroundings back. As w is the work done *on* the system then it will be negative in this case as in expanding, the gas is doing the work! Assuming for the moment the gas is an ideal gas then from the Ideal Gas Law we can obtain the integral below where n is the number of moles of gas in the system and R is the gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$pV = nRT \qquad p = \frac{nRT}{V} \qquad w = -\int \frac{nRT}{V} \, \mathrm{d}V$$

Find the work done when the gas expands from an initial volume V_i to a final volume V_f by integrating this equation.

Jump to Solution 3 (see page 111)

7.1.4 Question 4: Ideal Gas Expansion

We have one mole of ideal gas at an initial volume of $4.90 \times 10^3 \text{ cm}^3$ which expands to a final volume of $2.45 \times 10^4 \text{ cm}^3$ at a constant temperature $T = 298$ K. Using your solution from Question 3 calculate the work done *by* the gas due to this expansion.

Jump to Solution 4 (see page 112)

7.2 Week 7 Tutorial Solutions

7.2.1 Solution 1: Radioactive Decay

We are going to introduce the “separation of variables” method with this question and its solution.

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

(1) Treat $\mathrm{d}[\mathrm{A}]$ and $\mathrm{d}t$ as two separate variables which follow the normal rules of algebra (you *cannot* separate d from t as the operator d has to operate on something, this applies to any differential). (2) Rearrange the equation to bring everything that involves [A] to the left hand side and everything that involves t or are constants to the right hand side of the equation. (3) You can now integrate both sides of the equation separately, using the two appropriate sets of integration limits.

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k[\mathrm{A}] \qquad \frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -k\,\mathrm{d}t \qquad \int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = \int_0^t -k\,\mathrm{d}t$$

(4) Take any constants and negative signs outside of the integral for clarity, *i.e.* the rate constant k is independent of time and is constant. (5) The left and right hand sides of the equation are both standard integrals, the left hand side making use of the following standard integral

$$\int \frac{1}{x}\,\mathrm{d}x = \ln(x) + C$$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -k\int_0^t \mathrm{d}t \qquad \left[\ln[\mathrm{A}]\right]_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} = -k\left[t\right]_0^t$$

(6) This gives four alternative ways of writing the final definite integral and which one you use to solve a problem will depend upon the circumstances.

$$\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_0 = -kt \qquad \ln\left(\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0}\right) = -kt \qquad \frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = \mathrm{e}^{-kt} \qquad [\mathrm{A}]_t = [\mathrm{A}]_0\mathrm{e}^{-kt}$$

Return to Question 1 (see page 106)

7.2.2 Solution 2: Second-Order Chemical Reactions

Using the method of "separation of variables" for the integration of the second-order kinetics equation.

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

(1) Treat d[A] and dt as separate variables which follow the normal rules of algebra; then bring everything that involves [A] to the left hand side and everything that involves t or is a constant to the right hand side. (2) Now integrate both sides separately with the appropriate limits.

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

(3) An easy and foolproof way of integrating the left hand side of the equation is to write it as $[\mathrm{A}]^{-2}$ and then integrate as normal. You can use this "trick" to integrate many equations which at first sight might look a bit difficult.

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^2} = -k\,\mathrm{d}t \qquad \int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} [\mathrm{A}]^{-2}\,\mathrm{d}[\mathrm{A}] = -k\int_0^t \mathrm{d}t \qquad \left[\frac{[\mathrm{A}]^{-1}}{-1}\right]_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} = -k[t]_0^t$$

$$\left[\frac{-1}{[\mathrm{A}]}\right]_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} = -kt \qquad \frac{-1}{[\mathrm{A}]_t} - \frac{-1}{[\mathrm{A}]_0} = -kt$$

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

Return to Question 2 (see page 107)

7.2.3 Solution 3: Expanding Gas and Thermodynamic Work

$$w = -\int_{V_\mathrm{i}}^{V_\mathrm{f}} \frac{nRT}{V}\,\mathrm{d}V$$

Taking the constants outside the integral for clarity, the temperature of the gas T of the gas is constant and the number of moles of the system n is constant (gas in neither formed or lost), we may now integrate.

$$w = -nRT\int_{V_\mathrm{i}}^{V_\mathrm{f}} \frac{1}{V}\,\mathrm{d}V \qquad w = -nRT\left[\ln(V)\right]_{V_\mathrm{i}}^{V_\mathrm{f}}$$

$$w = -nRT\left(\ln(V_\mathrm{f}) - \ln(V_\mathrm{i})\right)$$

$$w = -nRT\,\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)$$

Return to Question 3 (see page 107)

7.2.4 Solution 4: Ideal Gas Expansion

The work done *on* the gas is calculated below.

$$w = -nRT\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)$$

$$w = -\left(1\ \mathrm{mol}\right)\left(8.314\ \mathrm{J\ K^{1}\ mol^{-1}}\right)\left(298\ \mathrm{K}\right)\ln\left(\frac{2.45\times10^{4}\ \mathrm{cm^3}}{4.90\times10^{3}\ \mathrm{cm^3}}\right)$$

$$w = -3.99\times10^{3}\ \mathrm{J} = -3.99\ \mathrm{kJ}$$

The work done *on* the gas is negative, which means the gas is doing work on the surroundings in the expansion process, the gas is "pushing back" the surroundings. The question was to calculate the work done *by* the gas in the expansion which is –*w*.

$$-w = +3.99\ \mathrm{kJ}$$

Return to Question 4 (see page 108)

8 Week 8: Chemistry and Integration 2

8.1 Week 8 Tutorial Questions

8.1.1 Question 1: Enthalpy of a Molecule and Temperature Changes

The enthalpy of a molecule, H, changes by dH when the temperature, T, changes by dT and the change is commonly given as a polynomial equation

$$\mathrm{d}H = \left(a + bT + cT^2\right)\mathrm{d}T$$

Calculate the change in the enthalpy, dH, of benzene (Fig. 8.1) when it is heated from 298 K to 398 K by integrating the polynomial given the following constants for benzene.

$a = -1.70\ \mathrm{J\ mol^{-1}\ K^{-1}}$ $b = 3.25\times10^{-1}\ \mathrm{J\ mol^{-1}\ K^{-2}}$ $c = 1.11\times10^{-4}\ \mathrm{J\ mol^{-1}\ K^{-3}}$

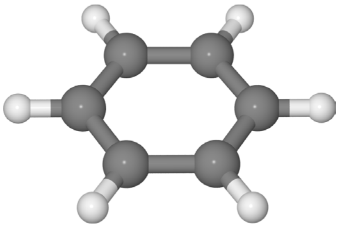


Figure 8.1: benzene molecule H = grey, C = dark grey.

Jump to Solution 1 (see page 116)

8.1.2 Question 2: Quantum Mechanics of a Conjugated Polyene Molecule

A polyene molecule is a linear hydrocarbon chain of alternating single and double bonded C-atoms. Polyene molecules are important in biological processes and Fig. 8.2 shows such a short polyene molecule.

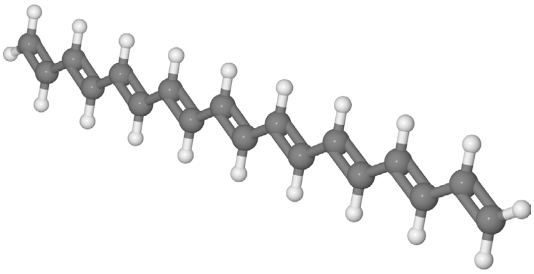


Figure 8.2: linear polyene molecule H = grey, C = dark grey

Because of the alternation of the single and double bonds, the π-electrons are *mobile* and may move along the length of the polyene. Thus we may treat the polyene molecule as a one-dimensional box of length L which confines the π-electrons. This interesting and important quantum mechanical concept will be discussed in your Chemistry degree. Fig. 8.3 shows some of the different wavefunctions for the allowed solutions for the mobile π-electrons as the quantum number n increases so does the energy of the π-electron in that level.

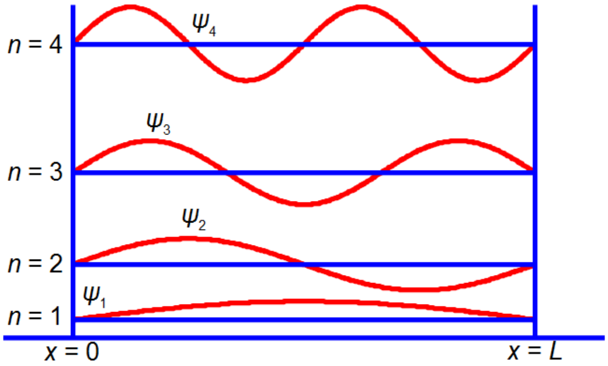


Figure 8.3: wavefunction for π-electrons in a polyene molecule.

The total probability of finding a π-electron at a certain position x, measured from one end of the one-dimensional box of length L is given below.

$$\int_0^L B^2 \sin^2\left(\frac{n\pi x}{L}\right) \mathrm{d}x = 1$$

Where the sine is in radians not degrees hence the need for π; x is the distance along the molecule from one end; n is a constant called a quantum number which may take any of the values $n = 1, 2, 3, \cdots$ and B is a constant to be evaluated. Use the standard integral below to integrate the probability equation from $x = 0$ to $x = L$ and thus find B in terms of L the length of the molecule (C is the constant of integration).

$$\int \sin^2(a\,x)\,\mathrm{d}x = \frac{x}{2} - \frac{\sin(2\,a\,x)}{4\,a} + C$$

Jump to Solution 2 (see page 117)

8.1.3 Question 3: The 1s Electron of the Hydrogen Atom

The probability P that an electron is a distance r from the nucleus is called the radial distribution function. The hydrogen atom's 1s electron radial distribution function is

$$P = \frac{4}{a_0^3} r^2 \mathrm{e}^{-\frac{2r}{a_0}}$$

Where a_0 is a constant called the Bohr radius (a_0 = 0.5292 Å or $a_0 = 0.5292 \times 10^{-10}$ m). Fig. 8.4 plots the hydrogen atom's 1s electron radial distribution function with a_0 = 0.5292 Å.

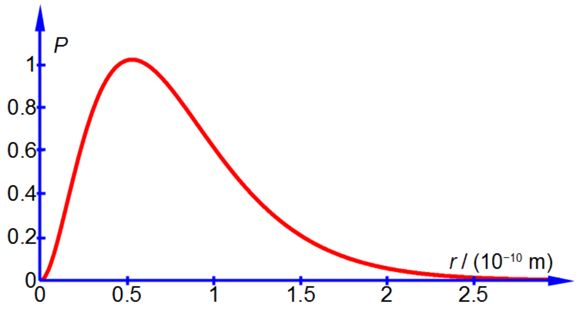


Figure 8.4: radial distribution function for the hydrogen 1s atomic orbital.

What is the probability of finding the electron at a radius of *less* than $2a_0$, *i.e.* integrate the above equation from $r = 0$ to $r = 2a_0$

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

Make use of the standard integral below.

$$\int x^2 \mathrm{e}^{bx} \mathrm{d}x = \mathrm{e}^{bx}\left(\frac{x^2}{b} - \frac{2x}{b^2} + \frac{2}{b^3}\right) + C$$

Jump to Solution 3 (see page 118)

8.2 Week 8 Tutorial Solutions

8.2.1 Solution 1: Enthalpy of a Molecule and Temperature Changes

Integrating from T_1 to T_2.

$$\mathrm{d}H = \left(a + bT + cT^2\right)\mathrm{d}T \qquad \int_{H_1}^{H_2} \mathrm{d}H = \int_{T_1}^{T_2} \left(a + bT + cT^2\right)\mathrm{d}T \qquad [H]_{H_1}^{H_2} = \left[aT + \frac{bT^2}{2} + \frac{cT^3}{3}\right]_{T_1}^{T_2}$$

$$H_2 - H_1 = \Delta H = a\left(T_2 - T_1\right) + \frac{b\left(T_2^{\,2} - T_1^{\,2}\right)}{2} + \frac{c\left(T_2^{\,3} - T_1^{\,3}\right)}{3}$$

For clarity of presentation, below I have split the evaluation of the integrated equation over two lines

$$\Delta H = \left(-1.70 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(398 \text{ K} - 298 \text{ K}\right) + \frac{\left(3.25\times10^{-1} \text{ J mol}^{-1} \text{ K}^{-2}\right)\left(\left(398 \text{ K}\right)^2 - \left(298 \text{ K}\right)^2\right)}{2} + \frac{\left(1.11\times10^{-4} \text{ J mol}^{-1} \text{ K}^{-3}\right)\left(\left(398 \text{ K}\right)^3 - \left(298 \text{ K}\right)^3\right)}{3}$$

$$\Delta H = \left(-1.70\times10^2 \text{ J mol}^{-1}\right) + \left(1.1310\times10^4 \text{ J mol}^{-1}\right) + \left(1.3535\times10^3 \text{ J mol}^{-1}\right)$$

$$\Delta H = 1.249\times10^4 \text{ J mol}^{-1}$$

$$\Delta H = 12.49 \text{ kJ mol}^{-1}$$

As a final step the enthalpy change of the benzene upon heating has been quoted in the conventional units of kJ mol^{-1}.

Return to Question 1 (see page 113)

8.2.2 Solution 2: Quantum Mechanics of a Conjugated Polyene Molecule

$$\int_0^L B^2 \sin^2\left(\frac{n\pi x}{L}\right) \mathrm{d}x = 1$$

Using the standard integral,

$$\int \sin^2(a x)\, \mathrm{d}x = \frac{x}{2} - \frac{\sin(2 a x)}{4a} + C$$

Take the constant B^2 outside the integral as B is not a function of x, let $a = n\pi/L$ in the standard integral gives

$$B^2\left[\frac{x}{2} - \frac{\sin\left(\frac{2n\pi x}{L}\right)}{\frac{4n\pi}{L}} + C\right]_0^L = 1$$

Substituting the limits $x = L$ and $x = 0$ and the constant of integration cancels out.

$$B^2\left(\frac{L}{2} - \frac{\sin\left(\frac{2n\pi L}{L}\right)}{\frac{4n\pi}{L}}\right) - B^2\left(\frac{0}{2} - \frac{\sin\left(\frac{2n\pi 0}{L}\right)}{\frac{4n\pi}{L}}\right) = 1$$

$$B^2\left(\frac{L}{2} - \frac{L\sin(2n\pi)}{4n\pi}\right) - B^2\left(0 - \frac{L\sin(0)}{4n\pi}\right) = 1$$

The term $2n\pi$ is in radians not degrees and as n is an integer, $\sin(2n\pi) = 0$, prove this by using your calculator to find $\sin(\pi)$ in radians. The second term of the upper limit is zero and both terms of the lower limit are also zero.

$$B^2\left(\frac{L}{2}\right) = 1 \qquad B^2 = \frac{2}{L}$$

$$B = \sqrt{\frac{2}{L}}$$

Although not directly part of the question, we now have the full equation for the wavefunctions of a π-electron in a given quantum level n of a polyene molecule as shown in Fig. 8.3.

$$\psi_n = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right)$$

Return to Question 2 (see page 113)

8.2.3 Solution 3: The 1s Electron of the Hydrogen Atom

The required probability comes from integrating the radial distribution function between $r = 0$ and $r = 2a_0$. Firstly, take the constant term $(4/a_0^3)$ outside the integral.

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

The integral is now recognizable in terms of the standard integral below.

$$\int x^2 \mathrm{e}^{bx}\,\mathrm{d}x = \mathrm{e}^{bx}\left(\frac{x^2}{b} - \frac{2x}{b^2} + \frac{2}{b^3}\right) + C$$

Using the substitutions $x = r$ and $b = -2/a_0$ and not forgetting the constant $(4/a_0^3)$, the probability integral is

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

The best way to deal with this complicated looking integral is to clean-up the denominators.

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

We now substitute in the two limits for our definite integral and the integration constant cancels out.

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

As $e^0 = 1$ and cancelling out terms we obtain

$$\mathrm{d}P = \frac{4}{a_0^3} e^{-4} \left(-\frac{13a_0^3}{4} \right) - \frac{4}{a_0^3} \left(\frac{-a_0^3}{4} \right)$$

$$\mathrm{d}P = -13e^{-4} + 1$$

$$\mathrm{d}P = 0.7619$$

So there is 0.7619 fractional probability (*i.e.* fraction of unity) that the electron will be within $2a_0$ of the nucleus for the 1s atomic orbital of the hydrogen atom. This is the same as saying there is a 76.19% chance that the 1s electron is between the nucleus and a distance of $2a_0$. See Fig. 8.4 for the radial distribution function and Fig. 8.5 for the 3-dimensional 1s atomic orbital drawn to enclose 90% of the total probability.

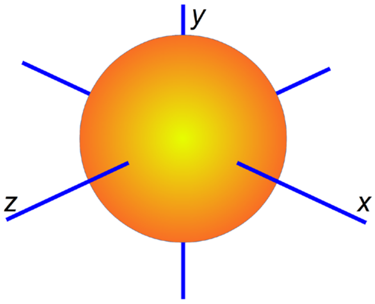


Figure 8.5: 1s atomic orbital.

Return to Question 3 (see page 114)

This workbook continues in *Intermediate Maths for Chemists* (Parker 2012) and *Advanced Maths for Chemists* (Parker 2013) which together cover a typical first year Maths course for your Chemistry (or a related) degree. Also the three books are very useful for *future reference* in later years of your degree(s). Go to my web page at http://johnericparker.wordpress.com/ for links to download the free textbooks.

9 References

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10 List of Formulae

These are a *sample* selection of the formulae encountered in *Introductory Maths for Chemists.*

Straight line $y = mx + c$ and graph plotting

Wave nature of light $c = \lambda\nu$ and the particle view of light $E = h\nu$

Chemical equilibrium $K_\mathrm{c} = \dfrac{[\mathrm{C}]^3[\mathrm{D}]^2}{[\mathrm{A}][\mathrm{B}]^2}$

Enthalpy of reaction and temperature change $\Delta H_2 - \Delta H_1 = C_p\left(T_2 - T_1\right)$

Kinetics of a complex reaction $v = \dfrac{k\,[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}{[\mathrm{Br_2}] + k'[\mathrm{HBr}]}$

van der Waals equation $\left(p + \dfrac{n^2 a}{V^2}\right)(V - nb) = nRT$

Vapour pressure of a liquid $\ln\left(\dfrac{p_2}{p_1}\right) = \dfrac{\Delta H^\circ_\mathrm{vap}}{R}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right)$

Binomial formula for abundances of isotopic compositions $\dbinom{n}{k} = \dfrac{n!}{k!\,(n-k)!}$

Lindemann treatment of a first-order “unimolecular” reaction $k_1[\mathrm{A}]^2 - k_2[\mathrm{A^*}][\mathrm{A}] - k_3[\mathrm{A^*}] = 0$

Rydberg equation $\bar{\nu} = R_\mathrm{H}\left(\dfrac{1}{n_1^{\,2}} - \dfrac{1}{n_2^{\,2}}\right)$

Bragg equation $n\lambda = 2d\sin(\theta)$

Polymer random coil $r^2 = Nl^2\dfrac{1 - \cos(\theta)}{1 + \cos(\theta)}$

Wavelength of a π-electron in a polyene $\psi(x) = A\cos(kx) + B\sin(kx)$

Acidity, alkalinity and the Henderson-Hasselbalch equation $\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\dfrac{[\mathrm{base}]}{[\mathrm{acid}]}\right)$

Quadratic formula $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Logarithms $b^c = a$ if b > 1 then $c = \log_b(a)$

Natural number $\mathrm{e}^x = 1 + x + \dfrac{x^2}{2!} + \dfrac{x^3}{3!} + \dfrac{x^4}{4!} + \cdots$

First-order and second-order kinetics $\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k[\mathrm{A}]$ and $\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k[\mathrm{A}]^2$

Arrhenius equation $k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}}$

Nernst equation for the Daniell cell $E = E^\mathrm{o} - \frac{RT}{nF}\ln\left(\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}\right)$

Gibbs free energy $\Delta G^\mathrm{o} = -RT\ln(K)$

Maxwell-Boltzmann distribution of speeds of molecules $f(c) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2 \mathrm{e}^{-\left(\frac{mc^2}{2kT}\right)}$

Differentiation of the Maxwell-Boltzmann equation and the most probable speed $c_\mathrm{mp} = \sqrt{\frac{2kT}{m}}$

Lennard-Jones equation $V = -4\varepsilon\left(\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right)$

Consecutive first-order chemical reactions $[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right)$

Expanding gas and thermodynamic work $w = -\int p\,\mathrm{d}V$

Quantum mechanics of a conjugated polyene molecule $\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$

Hydrogen atom 1s-electron radial distribution function $P = \frac{4}{a_0^3} r^2 \mathrm{e}^{-\frac{2r}{a_0}}$