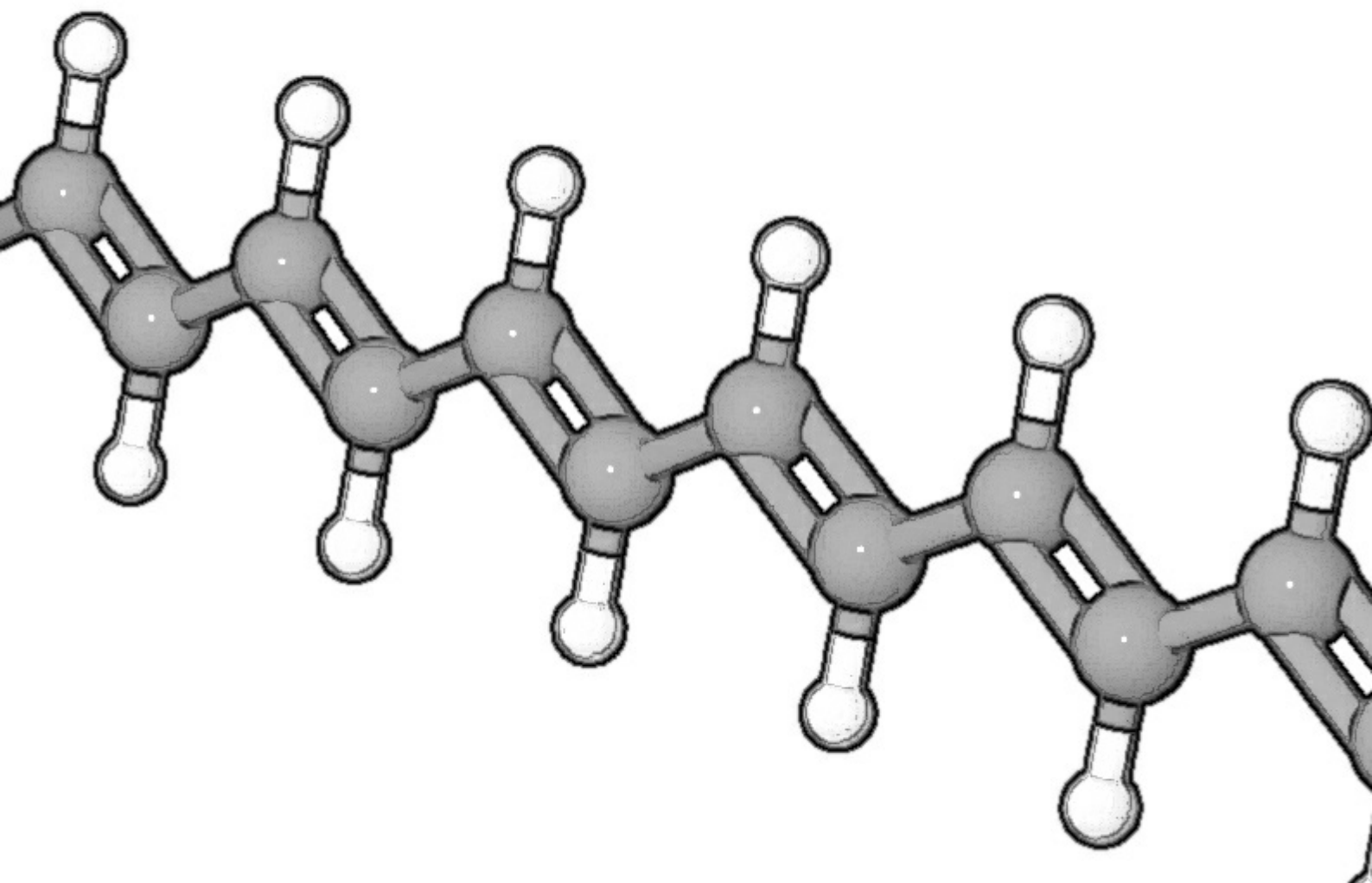


Introductory Maths for Chemists

Chemistry Maths 1

J. E. Parker



J.E. PARKER

INTRODUCTORY MATHS FOR CHEMISTS

CHEMISTRY MATHS 1

Introductory Maths for Chemists: Chemistry Maths 1

3rd edition

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I was pleased to respond to bookboon.com to write a textbook (which is split into 3 more manageable books, *Introductory Maths for Chemists*, *Intermediate Maths for Chemists*, and *Advanced Maths for Chemists* which should be studied in sequence) that would help chemistry students survive, and 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 Heriot-Watt University, Edinburgh, Scotland. These tutorials have formed the basis for these workbooks. I would like to thank the staff of Heriot-Watt University for their help; and thank the students who “suffered” these tutorials, I hope they helped them with their degrees and later careers. Most of all I would like to thank my wife Jennifer for her encouragement and help over many years.

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

Dr John Parker, BSc, PhD, CChem, FRSC
Honorary Associate Professor, Heriot-Watt University, Edinburgh.

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J.E.Parker@hw.ac.uk

<http://johnericparker.wordpress.com/>

ABOUT THE AUTHOR

Dr John Parker, PhD, BSc, CChem, FRSC

Honorary Associate Professor, Heriot-Watt University, Edinburgh

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

1 WEEK 1: CHEMISTRY AND ALGEBRA 1

1.1 INTRODUCTION

The three books; *Introductory Maths for Chemists*, (Parker 2018), *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, chemical engineering, chemical physics, molecular biology, biochemistry, or biology. From now on I will be using the term “chemistry” as a short-hand to cover chemical engineering, chemical physics, molecular biology, biochemistry, or biology as well as chemistry itself. The texts may also be very useful for final year school or college students prior to them starting an undergraduate degree and also to their chemistry teachers and lecturers. The text is published as three books in order to reduce file size and make handling on a laptop or tablet 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 chapters named as Week 1, Week 2, *etc.* This is *purely* to help you self-pace your work on a weekly basis.

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

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

1.1.1 WHY DO CHEMISTS HAVE TO DO MATHS?

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

1.1.2 HOW THE WORKBOOK IS STRUCTURED

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

1.1.3 PHYSICAL QUANTITIES

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 but 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 by mathematicians. But in science and engineering all the variables we use are *physical quantities*, such as mass, length, time, force, work, enthalpy, entropy, and so on. These physical quantities usually have a conventional symbol agreed by usage of the international community of scientists, for example, IUPAC the International Union of Pure and Applied Chemistry and IUPAP for physics. These symbols are used in the maths equations describing the phenomenon of interest. A few examples of the symbols used for physical quantities are m for mass, c for the velocity of light and E for energy. These come together in the equation that everyone has met, $E = mc^2$. In maths this is equivalent to $y = ax^2$ which could apply to many situations, however, $E = mc^2$ only applies to the specific process of 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.

$$\underbrace{c}_{\text{physical quantity}} = \underbrace{2.9979 \times 10^8}_{\text{pure number}} \underbrace{\text{m s}^{-1}}_{\text{units}} \quad \text{Definition: a physical quantity}$$

A physical quantity may be a *variable* or a *constant* they consist of two parts; a pure number (which in scientific notation may include a “multiplier” of ten raised to a power) and units. The pure number and the units are inseparable. An example would be $c = 2.9979 \times 10^8 \text{ m s}^{-1}$ where c is the symbol for the velocity of light. In order to clearly distinguish the three parts of the above equation, the symbol for physical quantity is written in italics (sloping) font and the number and the symbols for the units are in roman (upright) font. Don't worry too much about hand written material but for typed material it should be typed correctly.

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

1.1.4 LINEAR OR STRAIGHT LINE GRAPHS

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

$$y = mx + c \quad \text{Equation of a linear graph}$$

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 $x = 0$).

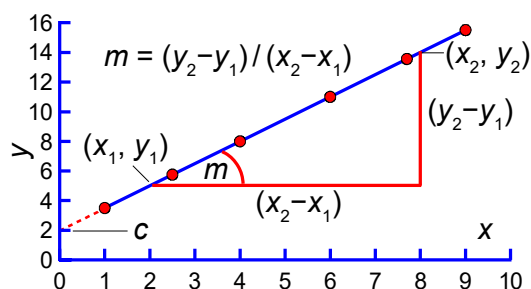


Figure 1.1: intercept and gradient for linear graph of $y = mx + c$.

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

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

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Where possible it is best to use a spreadsheet to plot the graph and find the equation of the line, both linear and non-linear least squares curve fitting are discussed in *Advanced Maths for Chemists* (Parker 2013). But you also need to be able to carry out the process by hand on graph paper, perhaps in an exam where computers, phones, and graphic calculators are normally not allowed except for some “open-book” type of exams, so practice with some of these tutorial questions! Once you have used your judgement to draw the best straight line *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 near the left hand side and near the right hand side of Fig. 1.1 $(x_1, y_1) = (2, 5)$ and $(x_2, y_2) = (8, 14)$.

(1) $5 = m \cdot 2 + c$	(2) $14 = m \cdot 8 + c$	Finding the equation of a linear graph
(3) $9 = m \cdot 6$	$m = 1.5$ (4) $19 = m \cdot 10 + 2c$	
(5) $19 = 1.5 \times 10 + 2c$	$c = 2$ (6) $y = 1.5x + 2.0$	

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

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

Graphs should be scaled so the data points fill most of the available space, the axes may not intersect at (0, 0) and the origin might be a long distance away from your data points. Do not extrapolate but find the equation of the best-fit straight line you draw.

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

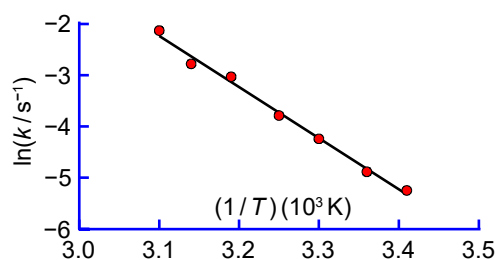


Figure 1.2: an Arrhenius plot.

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

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



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$$\begin{array}{lll}
 (7) \quad T = 300 \text{ K} & (8) \quad \frac{1}{T} = \frac{1}{300 \text{ K}} & (9) \quad \frac{1}{T} = 0.003333 \text{ K}^{-1} \\
 (10) \quad \frac{1}{T} = 3.333 \times 10^{-3} \text{ K}^{-1} & (11) \quad \frac{1/T}{10^{-3} \text{ K}^{-1}} = 3.333 & (12) \quad (1/T)(10^3 \text{ K}) = 3.333
 \end{array}$$

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

$$\begin{array}{ll}
 (13) \quad \overbrace{\ln(k/s^{-1})}^y = \overbrace{-9.98(10^3 \text{ K})}^m \overbrace{(1/T)}^x + \overbrace{28.7}^c & (14) \quad m = -9.98 \times 10^3 \text{ K} \\
 (15) \quad m = -\frac{E_a}{R} = -9.98 \times 10^3 \text{ K} & (16) \quad E_a = (9.98 \times 10^3 \text{ K})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \\
 (17) \quad E_a = 82.97 \times 10^3 \text{ J mol}^{-1} & (18) \quad E_a = 82.97 \text{ kJ mol}^{-1}
 \end{array}$$

The best-fit straight line equation of Fig. 1.2 is (13). In Section 3.1.1 on logs they are of pure numbers so in $\ln(k/s^{-1})$ the brackets cannot be separated out. Although the x -axis is written as $(1/T)(10^3 \text{ K})$ so that we can plot a small pure number however the gradient m is a physical quantity with a multiplier and units (14). For the Arrhenius equation we will discover later on that the gradient equals $-E_a/R$ where R is the gas constant and E_a is the activation energy (15). So cancelling out the negatives and taking the gas constant over to the right (16) we obtain the activation energy E_a (17) and (18) in the conventional units of kJ mol^{-1} .

$$(19) \quad c = 28.7 = \ln(A/s^{-1}) \quad (20) \quad A/s^{-1} = \exp(29.7) = 2.91 \times 10^{12} \quad (21) \quad A = 2.91 \times 10^{12} \text{ s}^{-1}$$

From the equation of the best-fit straight line for Fig. 1.2, the intercept $c = 28.7$ in (19). From the Arrhenius equation the intercept is $c = \ln(A/s^{-1})$. Don't worry if at the moment you are unsure of logs and antilogs as we will cover all of that area in Week 3 of this book. In (20) we take the antilog of the intercept. Only then may we take the units over to the right hand side to give the pre-exponential factor (21).

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 2013) very useful. Despite its name of *Engineering Mathematics* Stroud and Booth's book covers all the maths needed by *all* the sciences and engineering subjects. *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 2015) is excellent. For later on in your course the following textbooks have many examples of the interplay between chemistry and maths mainly in physical chemistry, Atkins, de Paula and Keeler 2017 and Atkins and de Paula 2016, and Levine 2009. For drawing and manipulating curves I use Graph 4.4.2 (Johansen 2013) which is an easy way of finding the areas under a curve between two limits, tangents, normals, and first and second differentials of a curve. I also use LibreOffice Writer, Calc spreadsheet, Draw, and Math for maths equations (LibreOffice 2018). For visualizing molecules I use Jmol (Jmol 2018). These three software packages are free.

1.2 WEEK 1 TUTORIAL QUESTIONS

Remember you should work out your own solution on paper *before* you 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. Fig. 1.3, light consists of a sine wave of electric field (E) and a sine wave of magnetic field (B) moving in phase together at right angles to one another and also at right angles to the direction of travel at the velocity of light (c), hence the alternative name for light of electromagnetic radiation. 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.

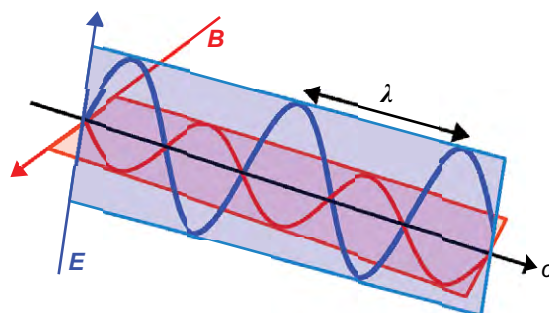


Figure 1.3: the oscillating electric and magnetic fields of light.

The wavelength λ (italic Greek “lambda”) is the distance between equivalent points on neighbouring waves, the units are sub-multiples of a metre. The correct symbol for frequency is ν (italic Greek “nu”) 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 (symbol Hz). The velocity of light $c = 2.9979 \times 10^8 \text{ m s}^{-1}$ is related to its wavelength and its frequency by the equation below. Calculate the wavelength λ of the light which is absorbed by a molecule if the light has a frequency of $\nu = 2.78 \times 10^{14} \text{ s}^{-1}$.

$$c = \lambda \nu \quad \text{Wavelength and frequency of light}$$

[Jump to Solution 1 \(see page 25\)](#)

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 $c \text{ mol L}^{-1}$ and is given in terms of the number of moles of the solute, $n \text{ mol}$, and the volume of the solution V measured in litres, symbol L. The IUPAC unit of volume is the metre cubed m^3 which is 1000 L, however, chemists often use the

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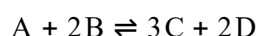
named sub-multiple unit litre as it is more convenient than the cubic metre and is identical to the decimetre cubed dm^3 .

$$c = \frac{n}{V} \quad \text{Definition: concentration in mol L}^{-1}$$

If 5 mL of a 0.1 mol L^{-1} aqueous solution is diluted by adding 10 mL of water, calculate the concentration of the new solution. Note that mL is the preferred symbol for millilitre or one thousandth of a litre L rather than ml which is still commonly seen on food and drinks labels and in health care.

[Jump to Solution 2 \(see page 26\)](#)

1.2.3 QUESTION 3: CHEMICAL EQUILIBRIUM



At a given temperature this reaction eventually comes to equilibrium. The double half-arrows or “dynamic equilibrium arrows” indicate that the reaction is at equilibrium, both the forward and the reverse reaction are still occurring simultaneously and the rates of the forward and reverse reactions have become equal to one another. 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 “standard concentration equilibrium constant” K_c° which is characteristic of the reaction at a given temperature. The concentration for example c_A may also be written as the molecule’s symbol inside square brackets [A] so $c_A = [\text{A}] \text{ mol L}^{-1}$.

$$\begin{array}{ll} c_A = [\text{A}] \text{ mol L}^{-1} & c_B = [\text{B}] \text{ mol L}^{-1} \\ c_C = [\text{C}] \text{ mol L}^{-1} & c_D = [\text{D}] \text{ mol L}^{-1} \end{array} \quad \text{Molar concentration}$$

At school or college you may have been told that equilibrium constants K_c° are dimensionless pure numbers, here is the reason. In the equation for the *standard* equilibrium constant K_c° each concentration is divided by its own *standard* state concentration. The two alternative symbols for the standard state is either a superscript “ \circ ” or a superscript “o” (pronounced “standard”). For solutes, their standard state concentrations are $c^\circ = 1 \text{ mol L}^{-1}$. As the concentration is divided by the standard concentration the units and the numerical value of “1” will cancel out to give the pure number “dimensionless concentrations” *e.g.* [A]. So K_c° the equilibrium constant must also be dimensionless. In chemical equilibria each of the concentrations is raised to the same power as its stoichiometric coefficient.

$$K_c^\circ = \frac{(c_C/c_C^\circ)^3 (c_D/c_D^\circ)^2}{(c_A/c_A^\circ) (c_B/c_B^\circ)^2} \quad K_c^\circ = \frac{([C] \text{ mol L}^{-1}/1 \text{ mol L}^{-1})^3 ([D] \text{ mol L}^{-1}/1 \text{ mol L}^{-1})^2}{([A] \text{ mol L}^{-1}/1 \text{ mol L}^{-1}) ([B] \text{ mol L}^{-1}/1 \text{ mol L}^{-1})^2}$$

$$K_c^\circ = \frac{[C]^3 [D]^2}{[A] [B]^2} \quad \text{Standard concentration equilibrium constant, a pure number}$$

- 1) Calculate the value of the equilibrium constant K_c° for the above equilibrium in a solution where all four of the concentrations are equal to 0.1 mol L^{-1} .
- 2) 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 \(see page 26\)](#)

1.2.4 QUESTION 4: ENTHALPY OF REACTION AND TEMPERATURE

At an initial temperature of T_1 the standard enthalpy change for a chemical reaction is $\Delta_r H_1^\circ$ and at the final temperature of T_2 it is $\Delta_r H_2^\circ$. 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 $\Delta_r H_2^\circ - \Delta_r H_1^\circ$.

$$\Delta_r H_2^\circ - \Delta_r H_1^\circ = \Delta_r C_p^\circ (T_2 - T_1)$$

The $\Delta_r C_p^\circ$ shows how sensitive the change in reaction enthalpy is to a change in temperature and $\Delta_r C_p^\circ$ is called the change of standard heat capacity at constant pressure for the chemical reaction. Over a *small* temperature change $\Delta_r C_p^\circ$ may be treated as constant. This last point is exemplified by Fig. 1.4 the graph of C_p° for N_2 against temperature where the tangent at 25°C shows that the heat capacity varies and can only be treated as a constant over a small range of temperatures.

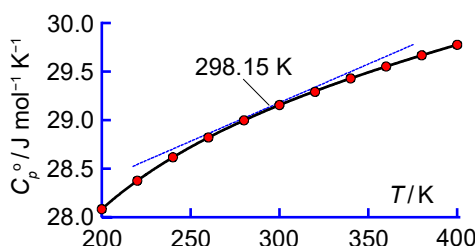


Figure 1.4: N_2 standard heat capacity at constant pressure.

Each of the reactants and products molecules of a reaction have a C_p° which will vary differently with T so the range of linearity for the reaction $\Delta_r C_p^\circ$ would be expected to be even smaller than that of a single molecule such as N_2 . With the above provision that the

linear relation between enthalpy of reaction and temperature is only valid over about a 60 °C range at the most, rearrange the above equation to get T_1 as the subject of the equation.

[Jump to Solution 4 \(see page 27\)](#)

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 gas by a complex (multi-step) chain reaction which will be covered in your chemical kinetics lectures.

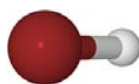


Figure 1.5: HBr molecule H (light grey) and Br (red).

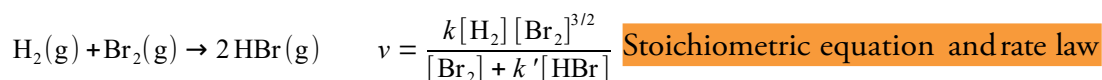
Studying the chemical kinetics of this reaction chemists found the rate of reaction (v) is given by the following rate law. The symbol v for rate of reaction (italic “vee” as in velocity) should *not* be confused with the Greek italic letter ν (“nu”), the context should remove any confusion.



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Where k and k' are parameters which depend upon the temperature of the reaction. Note that the stoichiometric coefficients are not related to the powers of the concentrations except for single-step “elementary reactions”. The concentration of *e.g.* H_2 is $[\text{H}_2]$ mol L⁻¹ but for clarity reaction rate equations are usually written without the units being explicitly shown.

Rearrange this equation for plotting as a straight line graph of $1/v$ against $[\text{HBr}]$ by taking reciprocals of both sides and simplifying the right hand side of the new equation to get the final form which is ready for a linear plot. What are the gradients and intercepts of this linear plot?

[Jump to Solution 5 \(see page 27\)](#)

1.2.6 QUESTION 6: NON-IDEAL GASES

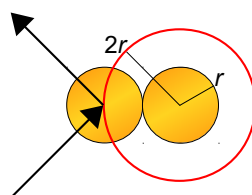


Figure 1.6: excluded volume.

The van der Waals equation models the behaviour of many non-ideal gases. Let us write the ideal gas law $pV = nRT$ in the form $p = nRT/V$. The ideal gas law assumes that the molecules have zero radii and do not attract or repel one another, the ideal gas law is clearly just a first approximation.

Let us look at the molecular repulsion. If the molecules have a van der Waals radius r due to electron-electron repulsion at short intermolecular distances, then around a molecule is an excluded volume, a sphere of radius $2r$ if all the molecules are identical. The volume V of the container of the gas molecules is reduced by nb where the empirical van der Waals parameter b reflects the “excluded volume” of a given species of molecule and n is the number of moles of gas. The ideal gas law is then modified to $p = nRT/(V-nb)$.

We also know that at long range molecules attract one another by van der Waals forces which are made up of contributions from London dispersion forces, permanent-dipole induced-dipole forces, and permanent-dipole permanent-dipole forces. These van der Waals attractive forces reduce the pressure of the gas in two ways, firstly by reducing the *frequency*

of collision between molecules, this reduction is proportional to the concentration of the molecules (n/V). The van der Waals forces secondly reduce the *force* of the collisions and hence reduce the gas pressure, this reduction is also proportional to the concentration (n/V). So the pressure of the gas is reduced in total by the long range forces by an^2/V^2 where “ a ” is the van der Waals parameter for the long-range attractive forces for a given molecule. This simple van der Waals treatment modifies the ideal gas law to the following expression with p as the subject. The van der Waals equation may also be written in a similar format to that of the ideal gas law.

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

Two versions of the van der Waals equation

An equation such as the van der Waals needs to be seen as a graph in order to be meaningful. Carbon dioxide has parameters $a = 3.64 \text{ L}^2 \text{ bar mol}^{-2}$ and $b = 0.04267 \text{ L mol}^{-1}$. Using the same units the gas constant is $R = 8.3145 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1}$, use a spreadsheet to plot the pressure p from 30 to 90 bar against the molar volume V_m from 0.07 to 0.3 L mol^{-1} for the following temperatures of 273.15, 298.15, 304.19, and 313.15 K. Comment upon the shapes of these curves, you will need to use a textbook to help formulate your comments.

[Jump to Solution 6 \(see page <?>\)](#)

1.2.7 QUESTION 7: VAPOUR PRESSURE OF LIQUIDS

When a volatile liquid or solid is placed into an evacuated container then some of the liquid evaporates or some of the solid sublimates into the gas phase. When the liquid or solid and its vapour have come to equilibrium at a temperature T the gas phase pressure is called the vapour pressure p .

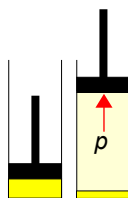


Figure 1.7: liquid or a volatile solid (left)
with its vapour at equilibrium (right).

Vapour pressure increases with increasing temperature. The enthalpy of vaporization $\Delta_{\text{vap}} H^\circ$ is the amount of heat required to vaporize a mole of liquid in its standard state. For a solid $\Delta_{\text{vap}} H^\circ$ is replaced by $\Delta_{\text{sub}} H^\circ$ the enthalpy of sublimation. The Clausius-Clapeyron equation

approximately models the change in vapour pressure with temperature for solid-gas or liquid-gas equilibria in which the vapour is not close to its critical temperature.

$$\frac{d \ln p}{dT} \approx \frac{\Delta_{\text{vap}} H^\circ}{RT^2} \quad \text{Clausius-Clapeyron equation}$$

The two approximations are firstly that the molar volume of a vapour is much larger than the molar volume of the liquid or solid so that the liquid or solid molar volumes can then be ignored. Secondly, that the vapour can be treated as an ideal gas except near its critical temperature. From the Clausius-Clapeyron equation if we assume that $\Delta_{\text{vap}} H^\circ$ is constant over a small temperature range then the equation may be integrated to give the equation below where T_1 and T_2 are low and high temperatures having vapour pressures p_1 and p_2 . Rearrange this equation to get T_2 as the subject of the equation.

$$\ln \frac{p_2}{p_1} \approx \frac{\Delta_{\text{vap}} H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

[Jump to Solution 7 \(see page 31\)](#)



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1.2.8 QUESTION 8: KINETICS OF A SECOND-ORDER CHEMICAL REACTION

An example of a second-order reaction (which depends upon a concentration squared) is the atmospheric reaction between nitric oxide NO and chlorine Cl₂. The superscript dot indicate a radical *i.e.* an unpaired electron. Nitrosyl chloride NOCl is a yellow gas first described in 1831.

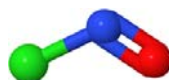
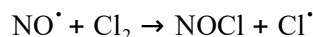
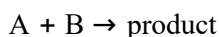


Figure 1.8: nitrosyl chloride N (blue), O (red) and Cl (green).

The rate of reaction of a second-order chemical reaction between two different reactants A and B depends on the concentrations of both the molecules A and B.



The rate of reaction is summarized by the rate law which includes the following term where a_0 and b_0 are the initial concentrations of molecules A and B, and x is the *change* in concentration of both reactants. Simplify this expression using partial fractions.

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

[Jump to Solution 8 \(see page 32\)](#)

1.2.9 QUESTION 9: ISOTOPE ABUNDANCES OF MOLECULES

$$\binom{n}{k} = \frac{n!}{k!(n-k)!} \quad \text{Definition: binomial theorem}$$

The shorthand notation which is on the left of the above equation is called the “binomial bracket”, there is no dividing line and it does *not* mean n divided by k . The binomial bracket is pronounced as “ n objects, choose k of them”. The exclamation mark such as in $n!$ is pronounced as “en factorial”.

$$n! = n(n-1)(n-2)(n-3)\cdots 1 \quad \text{Definition: the factorial of } n$$

There is only one arrangement of *zero* objects $0! = 1$ this is called the empty product by mathematicians. The symbol “...” means “the equation continues in the same way” it is

called an “ellipsis” and is the maths equivalent to “etc” in text. The binomial theorem is used in chemistry for: (1) calculating the intensities of NMR (nuclear magnetic resonance) lines due to spin-spin splitting, (2) in mass spectrometry for calculating the ion abundances (intensities) for molecules containing elements with several isotopes, (3) to model the biochemical transition between the helix and coiled structures of proteins, and (4) 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.

The binomial theorem expands the equation $(x + y)^n$ into a polynomial of terms ax^by^c where the powers b and c are positive integers and $n = b + c$. The coefficients “ a ” in the terms ax^by^c are known as the binomial coefficients. We already know $(x + y)^1 = x + y$ also that $(x + y)^2 = x^2 + 2xy + y^2$ and you should be able to work out for yourself by multiplying the last two equations together that $(x + y)^3 = x^3 + 3x^2y + 3y^2x + y^3$. The binomial coefficients of the terms in these three equations are respectively (1, 1) then (1, 2, 1) and (1, 3, 3, 1) if we carried on to $(x + y)^n$ then these binomial coefficients can be arranged in Pascal’s triangle where each entry is the sum of the two above it.

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1

Pascal’s triangle of binomial coefficients

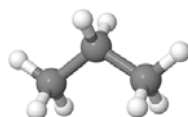


Figure 1.9: propane H (light grey) and C (dark grey).

The natural abundance of the stable carbon isotopes are about $^{13}\text{C} \approx 1\%$ and $^{12}\text{C} \approx 99\%$. 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 $^{13}\text{C}_3\text{H}_8$, $^{13}\text{C}_2^{12}\text{CH}_8$, $^{13}\text{C}^{12}\text{C}_2\text{H}_8$, and $^{12}\text{C}_3\text{H}_8$ these isotopic variants are called isotopologues.

[Jump to Solution 9 \(see page 33\)](#)

1.3 WEEK 1 TUTORIAL SOLUTIONS

1.3.1 SOLUTION 1: ELECTROMAGNETIC RADIATION AND MOLECULAR SPECTROSCOPY

$$\begin{aligned}
 (1) \quad c &= \lambda \nu & (2) \quad \frac{c}{\nu} &= \frac{\lambda \cancel{\nu}}{\cancel{\nu}} & (3) \quad \frac{c}{\nu} &= \lambda \\
 (4) \quad \lambda &= \frac{c}{\nu} & (5) \quad \lambda &= \frac{2.9979 \times 10^8 \text{ m s}^{-1}}{2.78 \times 10^{14} \cancel{\text{s}^{-1}}} & (6) \quad \lambda &= 1.0784 \times 10^{-6} \text{ m}
 \end{aligned}$$

Rearranging the equation (1) 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 to give (2). Cancelling top and bottom within any single term, ν (in red) cancels to give (3) and then rearranging (3) to make λ the subject (4). We say that λ is the subject of the equation (4) when it is on the left of the equal sign and it is equal to the rest of the equation. To make this physically meaningful we must substitute the physical quantities for the symbols (5) both numbers and units and then cancel the units within any single term. In this case it is s^{-1} that cancels (in red) to give (6) the wavelength with the units being *determined* by the correct use of physical quantities. The wavelength is in the near infrared part of the spectrum.

[Return to Question 1 \(see page 15\)](#)

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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 V and c vary. We rearrange the equation so that the unknown but constant quantity n becomes the subject of the equation and then substituting in the *original* physical quantities.

$$c = \frac{n}{V} \quad n = cV \quad n = (0.1 \text{ mol L}^{-1})(0.005 \text{ L}) \quad n = 5 \times 10^{-4} \text{ mol}$$

It is usually less confusing to carry out calculations in the base unit, here the litre (L), rather than in multiples or sub-multiples such as the mL. The volume of the diluted solution is 15 mL = 0.015 L. The diluted concentration may now be calculated.

$$c = \frac{n}{V} \quad c = \frac{5 \times 10^{-4} \text{ mol}}{0.015 \text{ L}} \quad c = 0.033 \text{ mol L}^{-1}$$

[Return to Question 2 \(see page 16\)](#)

1.3.3 SOLUTION 3: CHEMICAL EQUILIBRIUM

Firstly we need to calculate the value for the equilibrium constant.

$$K_c^\circ = \frac{[C]^3 [D]^2}{[A] [B]^2} \quad K_c^\circ = \frac{[0.1]^3 [0.1]^2}{[0.1] [0.1]^2} \quad K_c^\circ = 0.01$$

$$(1) \quad K_c^\circ = \frac{[C]^3 [D]^2}{[A] [B]^2} \quad (2) \quad K_c^\circ [A] [B]^2 = [C]^3 [D]^2 \quad (3) \quad \frac{K_c^\circ [A] [B]^2}{[D]^2} = [C]^3$$

$$(4) \quad [C]^3 = \frac{K_c^\circ [A] [B]^2}{[D]^2} \quad (5) \quad [C]^3 = \frac{0.01 \times 0.2 \times 0.15^2}{0.25^2} \quad (6) \quad [C]^3 = 7.2 \times 10^{-4}$$

$$(7) \quad [C] = 8.96 \times 10^{-2} \quad (8) \quad c_C = [C] \text{ mol L}^{-1} \quad (9) \quad c_C = 8.96 \times 10^{-2} \text{ mol L}^{-1}$$

The equilibrium constant equation (1) must be rearranged so that $[C]$ becomes the subject. First we multiply both sides of equation (1) by $[A][B]^2$ and then cancelling out top and bottom within any single term (not shown) to give (2). Divide both sides of (2) by $[D]^2$ and cancel top and bottom within any single term gives (3). Write $[C]^3$ as the subject in (4). In (5) substitute in the numerical value for K_c° and those for $[A]$, $[B]$, and $[D]$. We have in (6) the numerical value for $[C]^3$. Calculate in (7) the cube root of $[C]^3$ to find $[C]$. Remember (8) that $[C]$ is the symbol for the pure number of the concentration. The concentration (9) is thus $c_C = 8.96 \times 10^{-2} \text{ mol L}^{-1}$.

Increasing the concentrations of [A], [B], and [D] has *decreased* the concentrations of [C] in order to maintain the equilibrium constant K_c° at its constant value for the given temperature.

[Return to Question 3 \(see page 17\)](#)

1.3.4 SOLUTION 4: ENTHALPY OF REACTION AND TEMPERATURE

$$\begin{aligned} (1) \quad \Delta H_2^\circ - \Delta H_1^\circ &= \Delta C_p^\circ (T_2 - T_1) & (2) \quad \frac{\Delta H_2^\circ - \Delta H_1^\circ}{\Delta C_p^\circ} &= T_2 - T_1 \\ (3) \quad T_1 + \frac{\Delta H_2^\circ - \Delta H_1^\circ}{\Delta C_p^\circ} &= T_2 & (4) \quad T_1 &= T_2 - \frac{\Delta H_2^\circ - \Delta H_1^\circ}{\Delta C_p^\circ} \end{aligned}$$

(1) The lower temperature T_1 is inside the bracket. Remove the bracket (2) by dividing both sides by ΔC_p° . Add T_1 to both sides (3). Subtract $(\Delta H_2^\circ - \Delta H_1^\circ)/\Delta C_p^\circ$ from both sides (4) to make T_1 the subject of the equation.

[Return to Question 4 \(see page 18\)](#)

1.3.5 SOLUTION 5: KINETICS OF A COMPLEX CHEMICAL REACTION

$$\begin{aligned} (1) \quad v &= \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]} & (2) \quad \frac{1}{v} &= \frac{[\text{Br}_2] + k'[\text{HBr}]}{k[\text{H}_2][\text{Br}_2]^{3/2}} \\ (3) \quad \frac{1}{v} &= \frac{[\text{Br}_2]}{k[\text{H}_2][\text{Br}_2]^{3/2}} + \frac{k'[\text{HBr}]}{k[\text{H}_2][\text{Br}_2]^{3/2}} & (4) \quad \frac{1}{v} &= \frac{\overbrace{1}^c}{k[\text{H}_2][\text{Br}_2]^{1/2}} + \frac{\overbrace{k'}^m}{k[\text{H}_2][\text{Br}_2]^{3/2}} \overbrace{[\text{HBr}]}^x \end{aligned}$$

(1) This is the rate law for the reaction and in order to obtain a linear plot we use algebra as follows. (2) We take reciprocals on both sides of the equation. (3) The right hand term is split into two terms with the same denominator. The first of these two terms may then be simplified by cancelling out $[\text{Br}_2]$ top and bottom. (4) This is our linear graph with $y = 1/v$ and $x = [\text{HBr}]$ as in Fig 1.10.

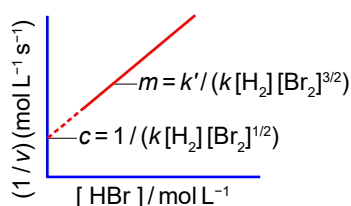


Figure 1.10: linear graph for $\text{H}_2 + \text{Br}_2 \rightarrow \text{HBr}$ reaction.

[Return to Question 5 \(see page 19\)](#)

1.3.6 SOLUTION 6: NON-IDEAL GASES

	A	B	C	D	E	F	G	H	I	J	K
		0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	31.04 °C	35 °C	40 °C
1	$V_m / \text{L mol}^{-1}$	p / bar	p / bar	p / bar	p / bar	p / bar	p / bar	p / bar	p / bar	p / bar	p / bar
2	0.0700	88.14	103.35	118.56	133.77	148.98	164.19	179.40	182.60	194.62	209.83
3	0.0701	87.22	102.38	117.54	132.69	147.85	163.00	178.16	181.34	193.32	208.47
4	0.0702	86.33	101.43	116.53	131.63	146.73	161.83	176.93	180.10	192.03	207.13

Table 1.1: the first few terms of the van der Waals spreadsheet.



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I am plotting more temperatures than asked for in the question as this is easy when using a spreadsheet. Table 1.1 shows the first few entries for the spreadsheet for drawing the van der Waals plots for CO₂ Fig. 1.11. The molar volumes in column A are typed in manually for a few of them and then selected and copied downwards by dragging the bottom-right handle of the selected cells in column A from 0.07 to 0.3 and then release the mouse button. The formulae for calculating the pressures are based upon the van der Waals equation with pressure as the subject $p = nRT/(V - nb) - an^2/V^2$. Remember the headings and all the cells of the spreadsheet are dimensionless pure numbers, *e.g.* the cell B2 formula is $=(0.083145*273.15)/(A2-0.04267)-(3.64/A2^2)$ which contains the two van der Waals parameters for CO₂ $a/L^2 \text{ bar mol}^{-2} = 3.64$ and $b/L \text{ mol}^{-1} = 0.04267$. The formulae in row 2 in typed in manually with temperatures in kelvin not degrees Celsius, and then selected and copied downwards by dragging the bottom-right handle to complete the spreadsheet.

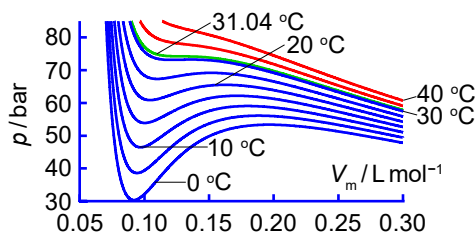


Figure 1.11: van der Waals plots for CO₂ at 5 °C intervals from 0 °C and 31.04 °C.

At temperatures below the critical temperature $T_c = 304.19 \text{ K}$ (31.04 °C) in green in Fig. 1.11 the van der Waals equation is giving unrealistic loops upwards then downwards called van der Waals loops. This is an artefact in the p - V plot due to the van der Waals equation only involves two terms in V_m and V_m^2 . Normally any given loop is replaced by a horizontal line so that the area of the downward loop cancels the area of the upward loop. This artefact is removed by using the virial equation $p = RT(1/V_m + B/V_m^2 + C/V_m^3 + \dots)$ which is at least a cubic equation in V_m with empirically derived virial coefficients B , C , *etc.* which are functions of temperature.

The van der Waals loops get smaller until they disappear as CO₂ approaches the critical temperature T_c of 31.04 °C. At the “critical point” CO₂ has a critical pressure of $p_c = 73.825 \text{ bar}$, a critical molar volume of $V_{m,c} = 0.092 \text{ L mol}^{-1}$ and a critical temperature of $T_c = 304.19 \text{ K}$ (Acree & Chickos 2017). The critical point is defined mathematically as a point of inflection that is where the first and second derivatives of the p - V curve are zero, below. A point of inflection is where a curve changes from a positive gradient to a negative gradient or the other way round. The curly Greek “delta” means the partial derivative with the variable temperature held constant. *Don’t* worry we will soon cover differentiation in this book.

$$\left(\frac{\partial p}{\partial V_m}\right)_T = 0 \quad \left(\frac{\partial^2 p}{\partial V_m^2}\right)_T = 0 \quad \text{Point of inflection in a curve of } p = f(V_m)$$

$$\begin{aligned} (1) \quad p_c &= \frac{RT_c}{V_{mc}-b} - \frac{a}{V_{mc}^2} & (2) \quad \frac{RT_c}{(V_{mc}-b)^2} &= \frac{2a}{V_{mc}^3} & (3) \quad \frac{RT_c}{(V_{mc}-b)^3} &= \frac{3a}{V_{mc}^4} \\ (4) \quad V_{mc}-b &= \frac{2V_{mc}}{3} & (5) \quad V_{mc} &= 3b & (6) \quad \frac{RT_c}{4b^2} &= \frac{2a}{27b^3} \\ (7) \quad T_c &= \frac{8a}{27Rb} & (8) \quad p_c &= \frac{8a}{27b} \left(\frac{1}{2b}\right) - \frac{a}{9b^2} & (9) \quad p_c &= \frac{a}{27b^2} \end{aligned}$$

Equations (1) is the van der Waals equation in term of the critical pressure p_c the critical temperature T_c and the critical molar volume V_{mc} . The first partial derivative set equal to zero and then rearranged is (2). The second partial derivatives set equal to zero and then rearranged is (3). These three simultaneous equations (1), (2), and (3) can be solved for the three unknowns p_c , V_{mc} , T_c the algebra for solving them is as follows. Equation (2) is divided by (3) to give (4) which rearranges to (5) with $V_{mc} = 3b$. Substitute critical molar volume from (5) $V_{mc} = 3b$ into equation (2) to give (6) which rearranges to (7) $T_c = 8a/27Rb$. Substituting the critical molar volume from (5) $V_{mc} = 3b$ and the critical temperature from (7) into the van der Waals equation (1) gives (8) which rearranges to (9) for the critical pressure $p_c = a/27b^2$.

The algebra of simultaneous equations has allowed us to find the critical values for the pressure, molar volume, and temperature from the van der Waals constants. Conversely, when experimental values for p_c and T_c are measured for a gas we can calculate the two van der Waals parameters “ a ” and “ b ” by solving the two simultaneous equations (7) and (9), you can prove this for yourself.

$$a = \frac{27R^2T_c^2}{64p_c} \quad b = \frac{RT_c}{8p_c} \quad \text{The van der Waals parameters from experimental } p_c \text{ and } T_c$$

Above the critical point the CO_2 is neither a gas nor a liquid but it is a “supercritical fluid”. Supercritical fluids have chemical and physical properties which are intermediate between those of a liquid and a gas, they are denser materials than what we would normally expect for a gas which gives them the ability to dissolve large nonvolatile molecules. CO_2 is an industrially important supercritical solvent which is easily recycled after use (by just lowering the pressure below p_c) and it is an environmentally friendly industrial technique as the CO_2 is a waste product of industry which is captured and reused and replaces organic solvents which may have environmental problems. Supercritical fluids are also used in supercritical chromatography for very efficient separation and analysis of nonvolatile mixtures.

[Return to Question 6 \(see page 20\)](#)

1.3 7 SOLUTION 7: VAPOUR PRESSURE OF LIQUIDS

This question is not as easy as it might first appear. The method suggested is one of several solutions but with this type of question it is easy to make a mistake, so a step by step approach is best.

$$\begin{aligned}
 (1) \quad \ln \frac{p_2}{p_1} &= \frac{\Delta_{\text{vap}} H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) & (2) \quad \ln \frac{p_2}{p_1} &= \frac{\Delta_{\text{vap}} H^\circ}{R T_1} - \frac{\Delta_{\text{vap}} H^\circ}{R T_2} \\
 (3) \quad \frac{\Delta_{\text{vap}} H^\circ}{R T_2} &= \frac{\Delta_{\text{vap}} H^\circ}{R T_1} - \ln \frac{p_2}{p_1} & (4) \quad \frac{1}{T_2} &= \frac{1}{T_1} - \frac{R \ln(p_2/p_1)}{\Delta_{\text{vap}} H^\circ} \\
 (5) \quad \frac{1}{T_2} &= \frac{\Delta_{\text{vap}} H^\circ - R T_1 \ln(p_2/p_1)}{T_1 \Delta_{\text{vap}} H^\circ} & (6) \quad T_2 &= \frac{T_1 \Delta_{\text{vap}} H^\circ}{\Delta_{\text{vap}} H^\circ - R T_1 \ln(p_2/p_1)}
 \end{aligned}$$

Starting with the variation of vapour pressure with temperature equation (1) then multiply out the brackets and cancel where possible gives (2). Rearrange (2) so that the term containing T_2 becomes the subject in (3). Divide by $\Delta_{\text{vap}} H^\circ/R$ throughout in (3) gives (4). Before we can take the reciprocal of we need to bring the right hand side of (4) to the common denominator of $T_1 \Delta_{\text{vap}} H^\circ$ as in (5). Finally we can now take reciprocals on both sides of equation (5) to give T_2 as the subject in (6).

[Return to Question 7 \(see page 21\)](#)



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1.3.8 SOLUTION 8: KINETICS OF A SECOND-ORDER CHEMICAL REACTION

In order to simplify the expression using partial fractions we use two undetermined coefficients A and B whose values we shall determine later on. In the partial fraction, note that the symbol “ \equiv ” means “identical to” and that an *identity* is true for *all* values of x . On the other hand, for an *equation* 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.

$$\frac{1}{(a_0-x)(b_0-x)} \equiv \frac{A}{(a_0-x)} + \frac{B}{(b_0-x)} \quad \text{Definition: partial fraction}$$

Multiply both sides of the identity above by $(a_0-x)(b_0-x)$ to give equation (1) and cancel out where possible gives (2). The identity (2) is true for *all* values of x and if we set $x = b_0$ as in (3) we find the unknown constant B in (4). Alternatively if we set $x = a_0$ in the identity (2) we have (5) which gives us the unknown constant A in (6). Note that the two unknown constants in (4) and (6) are $A = -B$.

$$(1) \quad \frac{(a_0-x)(b_0-x)}{(a_0-x)(b_0-x)} \equiv \frac{A(a_0-x)(b_0-x)}{(a_0-x)} + \frac{B(a_0-x)(b_0-x)}{(b_0-x)} \quad (2) \quad 1 \equiv A(b_0-x) + B(a_0-x)$$

$$(3) \quad 1 \equiv (A \times 0) + B(a_0 - b_0) \quad (4) \quad B \equiv \frac{1}{(a_0 - b_0)}$$

$$(5) \quad 1 \equiv A(b_0 - a_0) + (B \times 0) \quad (6) \quad A \equiv \frac{1}{(b_0 - a_0)}$$

Returning to our original partial fraction identity let us substitute for A and B for the partial fractions gives (7). Then in (8) we use brackets to clean up the right hand side of the solution of the partial fraction.

$$(7) \quad \frac{1}{(a_0-x)(b_0-x)} \equiv \frac{A}{(a_0-x)} + \frac{B}{(b_0-x)} \equiv \frac{1}{(b_0-a_0)(a_0-x)} - \frac{1}{(b_0-a_0)(b_0-x)}$$

$$(8) \quad \frac{1}{(a_0-x)(b_0-x)} \equiv \frac{1}{b_0-a_0} \left(\frac{1}{a_0-x} - \frac{1}{b_0-x} \right)$$

[Return to Question 8 \(see page 23\)](#)

1.3.9 SOLUTION 9: ISOTOPE ABUNDANCES OF MOLECULES

The carbon atom isotopic abundances in propane are found by expanding the binomial bracket below for the four different isotopologues with “3-C-atoms, choose 0, or 1, or 2, or 3” to be ^{12}C .

$$(1+99)^3 = \overbrace{\binom{3}{0} 99^0}^{0 \text{ } ^{12}\text{C}} + \overbrace{\binom{3}{1} 99^1}^{1 \text{ } ^{12}\text{C}} + \overbrace{\binom{3}{2} 99^2}^{2 \text{ } ^{12}\text{C}} + \overbrace{\binom{3}{3} 99^3}^{3 \text{ } ^{12}\text{C}}$$

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

$$(2) \quad (1+99)^3 = 1 + (3 \times 99) + (3 \times 99^2) + (1 \times 99^3)$$

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



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Expand the binomial bracket (1) using the binomial theorem. Cancelling out terms top and bottom gives (2) with the expected 1, 3, 3, 1 binomial coefficients for having 0, 1, 2, 3 ^{12}C atoms, that is the fourth row of Pascal's triangle. Multiplying by the 99 terms (the approximate percentage of ^{12}C) we obtain (3) the isotopologues abundancies.

Mathematically we have finished, but in chemistry the mass spectrometric abundances are normally expressed 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.

$^{13}\text{C}_3\text{H}_8$	$^{13}\text{C}_2\text{ }^{12}\text{CH}_8$	$^{13}\text{C }^{12}\text{C}_2\text{H}_8$	$^{12}\text{C}_3\text{H}_8$
1	297	29403	970299
0.00010 %	0.031 %	3.03 %	100 %

[Return to Question 9 \(see page 23\)](#)

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. In quantum mechanics one view of light is that it is made up of a stream of photons which are particles travelling at the speed of light (c). The energy of a single photon, E , is the product of Planck's constant $h = 6.6261 \times 10^{-34}$ J s and the frequency of the light. The accepted symbol for frequency is ν (italic Greek "nu"). Don't confuse frequency, italic Greek "nu" (the Greek "n") with the italic roman "vee", you can rely on the context to remove any confusion.

$$E = h\nu \quad \text{Photon energy}$$

The photon energy 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! Photons also have spin, as below.

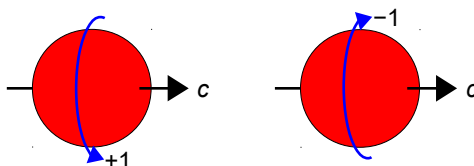


Figure 2.1: photons with right-handed (+1) and left-handed (-1) polarization.

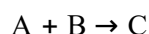
In section 1.2.1 we saw that quantum mechanics also views light as a wave, we have an equation that relates the frequency ν and the wavelength λ of light to the velocity of light $c = 2.9979 \times 10^8$ m s⁻¹.

$$c = \lambda\nu \quad \text{Wavelength and frequency of light}$$

Combine these two equations and calculate the energy of a single photon of wavelength $\lambda = 427$ nm (the symbol nm stands for a unit called a nanometre or 10^{-9} m).

[Jump to Solution 1 \(see page 48\)](#)

2.1.2 QUESTION 2: RATES OF CHEMICAL REACTIONS AND CONCENTRATIONS



This stoichiometric (the overall) reaction may have a mechanism consisting of several elementary steps. The experimental rate law for this reaction is 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. The rate of reaction v (italic roman “vee” as in velocity) is generally given in terms of the concentrations of the reacting species (indicated by square brackets) and the rate constant k . Purely for clarity in chemical kinetics it is conventional to indicate the concentration by just the pure number $[A]$ and not explicitly show the mol L⁻¹ units terms.

$$v = k \frac{[A]^2[B]^3}{[C]}$$

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

[Jump to Solution 2 \(see page 49\)](#)

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2.1.3 QUESTION 3: THE STRENGTH OF AN IONIC CRYSTAL STRUCTURE

An ionic crystal MX (M^+ being the metal cation and X^- the non-metal anion) is shown in Fig. 2.2, a small section of a KCl crystal.

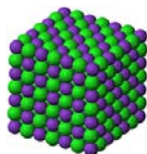
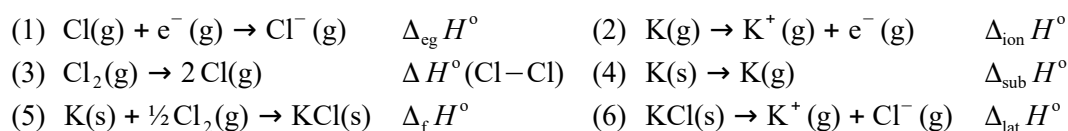


Figure 2.2: KCl crystal, K^+ (purple) and Cl^- (green).

The ionic crystal has a certain amount of intrinsic strength that holds the solid crystal structure together. This is called the lattice enthalpy $\Delta_{\text{lat}} H^\circ$ and is given by the equation of the Born-Haber cycle for KCl.

$$\Delta_{\text{lat}} H^\circ = -\Delta_f H^\circ + \Delta_{\text{sub}} H^\circ + \frac{1}{2} \Delta H^\circ(\text{Cl-Cl}) + \Delta_{\text{ion}} H^\circ + \Delta_{\text{eg}} H^\circ \quad \text{KCl Born-Haber cycle}$$



These enthalpy changes will be discussed early in your chemistry degree. The enthalpy changes are for: (1) electron gain of a chlorine atom in the gas phase, (2) ionization of a gaseous potassium atom, (3) bond dissociation of Cl_2 gas, (4) sublimation of solid potassium, (5) formation of KCl, and (6) the lattice energy of KCl.

Given the following data for potassium chloride crystals, rearrange the Born-Haber equation and calculate the electron gain enthalpy of chlorine.

$-\Delta_f H^\circ$	$\Delta_{\text{sub}} H^\circ$	$\Delta H^\circ(\text{Cl-Cl})$	$\Delta_{\text{ion}} H^\circ$	$\Delta_{\text{eg}} H^\circ$
-437 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 \(see page 50\)](#)

2.1.4 QUESTION 4: KINETICS OF ISOMERIZATION

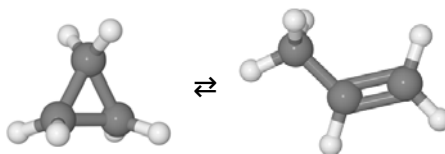
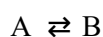
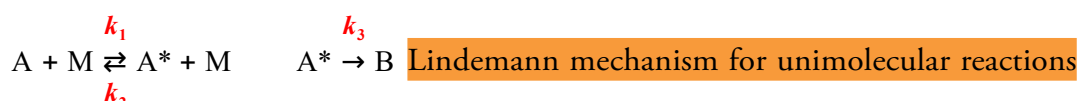


Figure 2.3: isomerization of cyclopropane to propene, H (light grey) and C (dark grey).

The double full-arrows indicate that the reactions may not necessarily have come to equilibrium but the reaction is reversible and can be started from either A or B molecules. Writing A for cyclopropane and B for propene for clarity, the Lindemann mechanism for the isomerization follows first-order kinetics in the concentration of A.



The Lindemann mechanism for first-order reaction mechanisms involves the collision between A and another molecule either A or B, let's call it M in general. This produces a highly vibrationally excited molecule A symbolized as A* which has enough energy to isomerize to B but it is not the transition state of the reaction. This is because the excitation energy of A* is dispersed over the vibrational modes of A*, 21 modes of vibration for cyclopropane. The energized molecule A* may do one of two things. If A* collides before it can isomerize it may lose enough vibrational energy that it can no longer isomerize, *i.e.* it has returned to a molecule A. Alternatively, if the energized molecule A* doesn't collide quickly, it may have enough *time* to isomerize to B by the vibrational energy accumulating into the transition state reaction coordinate.



Lindemann mechanism for unimolecular reactions

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During the algebraic manipulation of the three-step Lindemann mechanism the following kinetic equation is obtained.

$$k_1[A]^2 - k_2[A^*][A] - k_3[A^*] = 0$$

The square brackets indicate concentrations of the molecules A and A*. Rearrange the equation to get [A*] the concentration of the energized reactant as the subject. The rate of formation of the product B is from the mechanism $v = k_3[A^*]$, hence find the rate of reaction by substituting in your expression for [A*].

[Jump to Solution 4 \(see page 50\)](#)

2.1.5 QUESTION 5: ENTHALPY OF COMBUSTION OF BENZENE

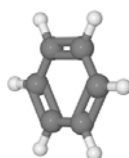
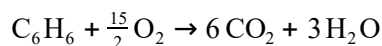


Figure 2.4: benzene, H (light grey) and C (dark grey).

Benzene combustion has the following stoichiometric reaction.



The standard reaction enthalpy $\Delta_r H^\circ$ is equal to the sum of the standard enthalpies of formation $\Delta_f H^\circ$ 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 n_i for that molecule. Enthalpy of formation is covered during your first year of your degree.

$$\Delta_r H^\circ = \sum n_i \Delta_f H^\circ(\text{products}) - \sum n_i \Delta_f H^\circ(\text{reactants})$$

Definition: standard reaction enthalpy

The standard enthalpy of combustion of benzene is shown below, rearrange the equation so that the enthalpy of formation of benzene is the subject.

$$\Delta_r H^\circ = 6 \Delta_f H^\circ(\text{CO}_2) + 3 \Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_f H^\circ(\text{C}_6\text{H}_6) - \frac{15}{2} \Delta_f H^\circ(\text{O}_2)$$

[Jump to Solution 5 \(see page 51\)](#)

2.1.6 QUESTION 6: HYDROGEN-ATOM SPECTROSCOPY

Fig. 2.5 is the visible Balmer spectrum that is observed for H-atoms when an electric discharge is passed through H₂ gas.

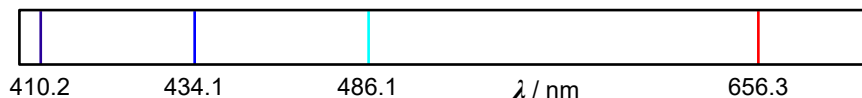


Figure 2.5: Balmer visible spectrum of the H-atom.

Wavelength is not directly proportional to the energy of the light ($E = h\nu$ and $c = \lambda\nu$ so $E = hc/\lambda$). The energy of light and of energy levels are normally quoted in terms of the wavenumber which is the reciprocal of wavelength when measured in centimetres. Wavenumber has a symbol $\bar{\nu}$ (italic Greek “nu” with a bar over the top, pronounced “nu bar”). The wavenumber of light is the number of light waves per centimetre, with units of cm^{-1} pronounced as “centimetres to the minus one” or “reciprocal centimetres”, see Fig. 2.6.

$$\bar{\nu} \text{ cm}^{-1} = \frac{1}{\lambda \text{ cm}} \quad \text{Definition: wavenumber}$$

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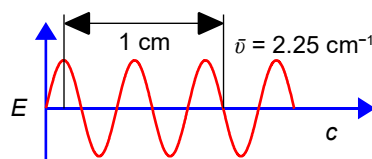


Figure 2.6: an example of the wavenumber (cm^{-1}) of light.

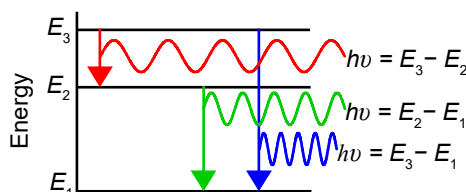


Figure 2.7: Bohr model of light emission as jumps between quantum states.

The quantized energy levels are called atomic orbitals (AOs) and for the H-atom are characterized by the principal quantum numbers, $n = 1, 2, 3, \dots \infty$ where the infinite energy level corresponds to ionization of the H-atom. The Bohr model for light emission is the transition from n_2 to n_1 and for light absorption from n_1 to n_2 where the energy of $n_2 > n_1$. In Fig. 2.5 the Balmer visible spectrum are transitions down to $n_1 = 2$.

$$\bar{\nu} = R_{\text{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{Rydberg equation for H-atom electronic spectra}$$

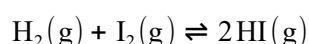
The Rydberg equation accurately summarizes the UV-visible electronic spectrum of H-atoms. It gives the wavenumber of the light emitted or absorbed where the Rydberg constant is $R_{\text{H}} = 109677 \text{ cm}^{-1}$. Rearrange the Rydberg equation to obtain n_2 as the subject.

[Jump to Solution 6 \(see page 51\)](#)

2.1.7 QUESTION 7: CHEMICAL EQUILIBRIUM AND CONCENTRATION CALCULATIONS



Figure 2.8: hydrogen iodide H (grey) and I (purple).



The above chemical reaction when carried out at a temperature of 425°C has not only the H_2 but also the I_2 and HI all in the gas phase. The chemical symbol of the “two half-arrows” indicates that the reaction is at a *dynamic equilibrium*, the reaction is going in both

directions simultaneously with equal rates of reaction. This reaction has an equilibrium constant $K_c^\circ = 55.64$ at 425 °C (see section 1.2.3 for a discussion about dimensionless equilibrium constants). If we originally placed 2 mol L⁻¹ of H₂ and 2 mol L⁻¹ of I₂ in a flask at 425 °C with no HI present, calculate the equilibrium concentrations of H₂, I₂ and HI when equilibrium is achieved at 425 °C.

$$K_c^\circ = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 55.64$$

The way to tackle this type of question is to assume that x moles of H₂ and I₂ are consumed in going from the original conditions to equilibrium and $2x$ moles of HI are formed when equilibrium is achieved. The concentrations at equilibrium are then shown below.

$$\overbrace{\text{H}_2}^{[2-x]} + \overbrace{\text{I}_2}^{[2-x]} \rightleftharpoons \overbrace{2\text{HI}}^{[2x]} \quad K_c^\circ = \frac{[2x]^2}{[2-x][2-x]} = 55.64$$

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, calculate the equilibrium concentrations for the three species of molecule.

[Jump to Solution 7 \(see page 52\)](#)

2.1.8 QUESTION 8: CRYSTAL STRUCTURES BY X-RAY DIFFRACTION

When a molecule forms a crystalline solid we can use a beam of monochromatic X-rays to determine the positions of *equivalent* atoms within the crystal *i.e.* the same atom within the identical molecules making up the crystal. X-rays are very short wavelength light with wavelengths of a few ångströms ($\text{\AA} = 10^{-10} \text{ m}$) which are of the order of the spacing between equivalent atoms in crystals.

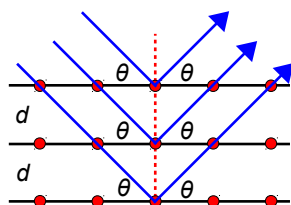


Figure 2.9: X-rays being diffracted by crystal planes of equivalent atoms.

The crystal consists of equally spaced planes of *equivalent* atoms, each of which may be part of a large molecule. Most of the X-rays pass through the crystal without any interaction.

Some X-rays interact with the planes of equivalent atoms but will have different path-lengths depending upon which plane of atoms “reflect” them. These different path-length X-rays will interfere, mainly in a destructive manner. A small number of photons will have a path-length difference of $2d \sin(\theta)$ equal to an integral multiple n of the wavelength λ of the X-rays and they constructively interfere and give a diffraction pattern. Clearly the path-length difference depends upon the angle of incidence θ of the X-rays to the planes of atoms the crystal and the distance between the planes of atoms d (called the lattice spacing).

$$2d \sin \theta = n\lambda \quad n = 1, 2, 3, \dots \quad \text{The Bragg equation for X-ray diffraction}$$

Where $n = 1, 2, 3, \dots$ is the order of the diffraction and is a dimensionless number. Calculate the lattice spacing d when using radiation of wavelength $\lambda = 0.154 \text{ nm}$ for $n = 1$ (called a first-order reflection) at a scattering angle of $\theta = 11^\circ$. Specify the units for your calculated d value.

[Jump to Solution 8 \(see page 53\)](#)

2.1.9 QUESTION 9: POLYMER CHEMISTRY

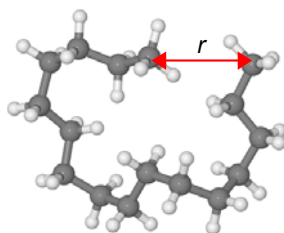


Figure 2.10: a short randomly coiled polyethylene, H (light grey) and C (dark grey).

Long polymer molecules tend to coil up rather than being stretched out straight, Fig. 2.10 is an example of a short polythene (polyethylene) molecule. Averaging a large number of such randomly coiled molecules the average end-to-end distance $\langle r \rangle$ of the polymer molecules is given below. The angled brackets in $\langle r \rangle$ is the normal way of indicating the mean or average of the quantity inside the brackets.

$$\langle r \rangle^2 = Nl^2 \frac{1 - \cos \theta}{1 + \cos \theta} \quad \text{Average end-to-end distance } \langle r \rangle \text{ of an ideal random coil polymer}$$

The polymer consists of N chemical bonds making up the backbone of the polymer chain, with a monomer length of l , and θ is the C-C-C atom bond angle. Calculate the average

end-to-end distance $\langle r \rangle$ for a polymer with $\theta = 109.5^\circ$ (the tetrahedral angle), $l = 154 \text{ pm}$, and $N = 5 \times 10^3$. Specify the units for your calculated $\langle r \rangle$ value.

[Jump to Solution 9 \(see page 53\)](#)

2.1.10 QUESTION 10: CONJUGATED MOLECULES AND QUANTUM CHEMISTRY

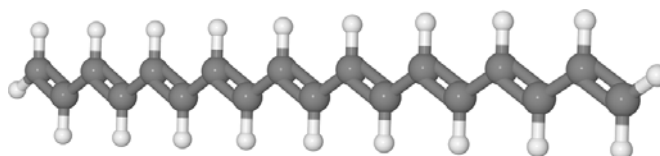


Figure 2.11: a polyene conjugated molecule H (light grey) and C (dark grey).

A conjugated molecule is one with alternating single and double carbon-carbon bonds in its backbone. Conjugated molecules are important parts of large biological molecules for many different functions including your ability to detect light within your eyes' retina and for plant photosynthesis. Conjugated molecules are important industrial dyes. A simple example of a conjugated molecule is a "linear" polyene, Fig.2.11. The quantum mechanical equation



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for the π -electrons in a simple 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 (Parker 2015, section 1.7.2 and Parker 2016, section 1.7).

$$\psi(x) = A\cos(kx) + B\sin(kx) \quad \text{General wavefunction that applies to all wave motion}$$

Where A , B , and k are constants whose values need to be determined for the polyene molecule and the sine and cosine functions are in *radians* not degrees. Find the constant k and any constraints that A or B may have using the boundary conditions that at the two ends of the polyene molecule the wavefunctions must be zero in order to have the electron confined within the polyene, $\psi(0) = 0$ and $\psi(L) = 0$.

[Jump to Solution 10 \(see page 54\)](#)

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.

[Jump to Solution 11 \(see page 55\)](#)

2.1.12 QUESTION 12: WEAK ACIDS

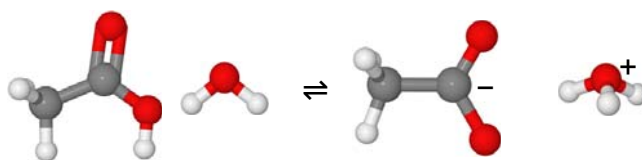
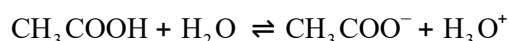


Figure 2.13: acetic acid, water, acetate ion, and hydronium ion.

Acetic acid (ethanoic acid) is a weak acid which partially dissociates in water to the acetate ion and hydronium ion. The standard equilibrium constant is K_a° (“a” is for acid). See section 1.2.3 for a discussion about dimensionless equilibrium constants.

$$K_a^\circ = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$$

The solvent water is in a large excess and to a very good approximation its concentration is constant. We can incorporate $[H_2O]$ with the standard equilibrium constant K_a° to give the “acidity constant” $K_a = K_a^\circ [H_2O]$.

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

Acetic acid acidity constant K_a

Acetic acid's acidity constant is $K_a = 1.7539 \times 10^{-5}$ at 298.15 K. Calculate the hydronium ion concentration $[H_3O^+]$ for a 0.15 mol L^{-1} solution of acetic acid? We can solve 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 ions and hydronium ions.

$$1.7539 \times 10^{-5} = \frac{x^2}{0.15 - x}$$

This chemical equilibrium problem has been reduced to solving the quadratic equation written in the standard form $ax^2 + bx + c = 0$ using the quadratic formula.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

The quadratic formula

[Jump to Solution 12 \(see page 56\)](#)



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2.1.13 QUESTION 13: THE SYNTHESIS OF AMMONIA

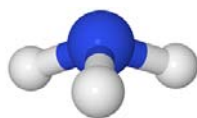
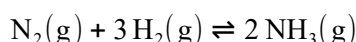


Figure 2.14: ammonia N (blue) and H (light grey).

Ammonia is an important industrial chemical as a starting material for many other compounds including fertilizer, nitric acid, urea, and ammonium nitrate. Ammonia is synthesized using the following equilibrium reaction where the reactant and products are in the gas-phase.



It makes sense to define the standard pressure equilibrium constant K_p° in terms of the partial pressures of the gases at equilibrium, which is $K_p^\circ = 1.64 \times 10^{-4}$ at 400 °C.

$$K_p^\circ = \frac{[p(\text{NH}_3)_{\text{eq}}/p^\circ]^2}{[p(\text{N}_2)_{\text{eq}}/p^\circ][p(\text{H}_2)_{\text{eq}}/p^\circ]^3}$$

Ammonia standard pressure equilibrium constant

K_p° is given in terms of the partial pressures of the reactants and products in pascals or bars where each partial pressure is divided by the standard pressure of $p^\circ = 1 \times 10^5$ Pa or $p^\circ = 1$ bar and K_p° is dimensionless. Each of the terms is raised to the power of its stoichiometric coefficient. As the standard pressure base unit in pascals is not unity $p^\circ = 1 \times 10^5$ Pa and appears in each of the p° terms it affects the value for K_p° , and we cannot make a simplification similar to the one we made for K_c° in terms of concentration where $c^\circ = 1 \text{ mol L}^{-1}$ (see section 1.2.3). For any given equilibrium reaction each K_p° in terms of partial pressures in pascals must be written in full with the p° values included. This suggests that it is better to use the standard pressure $p^\circ = 1$ bar (which is unity) rather than 1×10^5 Pa and that *all* the pressures are also quoted in bar we can then cancel out the units “bar” and greatly simplify the arithmetic!

For our reaction we initially have partial pressures of $p_{\text{N}_2} = 1$ bar and $p_{\text{H}_2} = 3$ bar of H_2 which are mixed, there being no NH_3 present and the mixture is allowed to come to equilibrium at 400 °C. If x is the fraction of a mole of N_2 which is lost due to the reaction then the equilibrium constant becomes as below.

$$\overbrace{\text{N}_2(\text{g})}^{(1-x)} + 3 \overbrace{\text{H}_2(\text{g})}^{(3-3x)} \rightleftharpoons 2 \overbrace{\text{NH}_3(\text{g})}^{(2x)} \quad K_p^\circ = \frac{[2x]^2}{[1-x][3-3x]^3} = 1.64 \times 10^{-4}$$

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 $(3-3x)$ and remember that each term is raised to the power of its stoichiometric coefficient.

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

[Jump to Solution 13 \(see page 57\)](#)

2.2 WEEK 2 TUTORIAL SOLUTIONS

2.2.1 SOLUTION 1: ENERGY OF A SINGLE PHOTON

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

The common variable in these two equations is the frequency ν . The energy of a single photon is found by: rearranging $c = \lambda \nu$ to get ν as the subject $\nu = c/\lambda$, substituting this expression for ν into $E = h\nu$ gives $E = hc/\lambda$.

$$\begin{aligned} (1) \quad E &= \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{427 \times 10^{-9} \text{ m}} & (2) \quad E &= 4.652 \times 10^{-19} \text{ J} \\ (3) \quad E &= (4.652 \times 10^{-19} \text{ J})(6.0221 \times 10^{23} \text{ mol}^{-1}) = 280100 \text{ J mol}^{-1} & (4) \quad E &= 280.1 \text{ kJ mol}^{-1} \end{aligned}$$

(1) Substitute the physical quantities into $E = hc/\lambda$ note that in the calculation we have replaced nanometres by the base units metres in order that the units cancel. (2) The energy of a *single* photon is incredibly *small*, the power of -19 is a minute fraction of a joule, and one joule is about the energy required to lift a medium-size tomato (100 g) 1 m vertically from the surface of the Earth. (3) In practice we normally only meet photons in enormous numbers (a mole of photons) which can give chemically significant amounts of total energy of hundreds of kJ of light energy. A mole of photons is called an einstein (note the lower case “e” for the named unit, the 1921 Nobel Prize winner Einstein is an upper case “E”). (4) An einstein of 427 nm photons is 280 kJ which for comparison is of the order of magnitude of the Cl-Cl bond dissociation energy of 242 kJ mol $^{-1}$.

[Return to Question 1 \(see page 35\)](#)

2.2.2 SOLUTION 2: RATES OF CHEMICAL REACTIONS AND CONCENTRATIONS

$$\begin{aligned} (1) \quad v_{\text{initial}} &= k \frac{[A]^2[B]^3}{[C]} & (2) \quad v_{\text{final}} &= k \frac{[2A]^2[2B]^3}{[2C]} & (3) \quad v_{\text{final}} &= k \frac{4[A]^2 8[B]^3}{2[C]} \\ (4) \quad v_{\text{final}} &= 16k \frac{[A]^2[B]^3}{[C]} & (5) \quad v_{\text{final}} &= 16v_{\text{initial}} & (6) \quad \frac{v_{\text{final}}}{v_{\text{initial}}} &= 16 \end{aligned}$$

(1) the original rate law. (2) The final rate law with the powers applying to the new *doubled* concentrations. (3) and (4) Take the numeric factors outside the brackets. (5) Replace the bracketed terms with the initial rate law. (6) Doubling all the concentrations has made this particular reaction go 16 times faster.

[Return to Question 2 \(see page 36\)](#)

2.2.3 SOLUTION 3: THE STRENGTH OF AN IONIC CRYSTAL STRUCTURE

$$\begin{aligned} (1) \quad \Delta_{\text{lat}} H^\circ &= -\Delta_{\text{f}} H^\circ + \Delta_{\text{sub}} H^\circ + \frac{1}{2} \Delta H^\circ(\text{Cl-Cl}) + \Delta_{\text{ion}} H^\circ + \Delta_{\text{cg}} H^\circ \\ (2) \quad \Delta_{\text{cg}} H^\circ &= \Delta_{\text{lat}} H^\circ + \Delta_{\text{f}} H^\circ - \Delta_{\text{sub}} H^\circ - \frac{1}{2} \Delta H^\circ(\text{Cl-Cl}) - \Delta_{\text{ion}} H^\circ \\ (3) \quad \Delta_{\text{cg}} H^\circ &= (+717 + (-437) - (+89) - \frac{1}{2}(+244) - (+418)) \text{ kJ mol}^{-1} \\ (4) \quad \Delta_{\text{cg}} H^\circ &= (+717 - 437 - 89 - \frac{1}{2} \times 244 - 418) \text{ kJ mol}^{-1} \\ (5) \quad \Delta_{\text{cg}} H^\circ &= -349 \text{ kJ mol}^{-1} \end{aligned}$$

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(1) The lattice enthalpy equation is rearranged to give (2) with the electron gain enthalpy as the subject of the equation. (3) Substitute the physical quantities for the symbols, note the difference between the mathematical *operations* of addition or subtraction as shown by plus or minus signs with a space before the number, and the positive or negative *values* of the physical quantities themselves shown by plus or minus *without* a space before the number. (4) Multiply out the brackets. (5) The value for the electron gain enthalpy $\Delta_{\text{eg}} H^\circ = -349 \text{ kJ mol}^{-1}$ means the reaction $\text{Cl(g)} + \text{e}^-(\text{g}) \rightarrow \text{Cl}^-(\text{g})$ is exothermic, that is the isolated chloride ion is more stable than the isolated chlorine atom and electron, all in the gas phase. Also there is in the literature the term “electron affinity” E_{ea} which is the energy *released* in the above reaction. The word “released” means that for the exothermic reaction is written as $E_{\text{ea}} = +349 \text{ kJ mol}^{-1}$.

[Return to Question 3 \(see page 37\)](#)

2.2.4 SOLUTION 4: KINETICS OF ISOMERIZATION

$$\begin{array}{ll}
 (1) \quad k_1[A]^2 - k_2[A^*][A] - k_3[A^*] = 0 & (2) \quad -k_2[A^*][A] - k_3[A^*] = -k_1[A]^2 \\
 (3) \quad k_2[A^*][A] + k_3[A^*] = k_1[A]^2 & (4) \quad [A^*](k_2[A] + k_3) = k_1[A]^2 \\
 (5) \quad [A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} & (6) \quad v = k_3[A^*] \\
 (7) \quad v = \frac{k_3 k_1[A]^2}{k_2[A] + k_3} & (8) \quad v \approx \frac{k_3 k_1[A]^2}{k_2[A]}
 \end{array}$$

Starting with the original kinetics equation (1) we move the term which does *not* involve $[A^*]$ to the right hand side by subtracting $k_1[A]^2$ from both sides, (2). Multiply (2) throughout by -1 to make all three terms positive, (3). Take $[A^*]$ outside a bracket in (4) for the two terms on the left hand side. (5) Divide left and right by $(k_2[A] + k_3)$. The rate of reaction in (6) is $k_3[A^*]$, so (7) is the exact rate of reaction but can we approximate it?

Looking at the left hand side of (3) the $[A^*] \ll [A]$ so $k_3[A^*] \ll k_2[A^*][A]$ which cancelling out $[A^*]$ in this inequality gives $k_3 \ll k_2[A]$. We can now approximate the exact rate of reaction (7) by ignoring the negligible term k_3 in the denominator we get the approximation for the rate in (8). For this approximate rate (8) we may *now* cancel out the $[A]$ in the denominator with the square term to obtain a good approximation for the rate of isomerization.

$$v \approx \frac{k_3 k_1}{k_2} [A] \quad \text{Lindemann rate of “unimolecular” isomerization reactions}$$

Notice there is a difference between approximating an expression and incorrect algebraic cancellations. In (5) we *cannot* cancel out the variable $[A]$ top and bottom to do so is a common mistake. 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, look at the numeric example below.

$$\frac{2}{2 \times 3 + 3} = \frac{2}{9} \quad \frac{2}{2 \times 3 + 3} \neq \frac{1}{6}$$

[Return to Question 4 \(see page 37\)](#)

2.2.5 SOLUTION 5: ENTHALPY OF COMBUSTION OF BENZENE

This question is very simple but might look complicated by the size of the enthalpy symbols. In (1) take $\Delta_f H^\circ(\text{C}_6\text{H}_6)$ over to the left hand side to give (2) by adding $\Delta_f H^\circ(\text{C}_6\text{H}_6)$ to both sides of the equation and cancelling out. Take the enthalpy of combustion $\Delta_r H^\circ$ in (2) to the right hand side to give (3) by subtracting $\Delta_r H^\circ$ from both sides and then cancelling out. The enthalpy of formation for benzene is the subject of equation in (3).

$$(1) \quad \Delta_r H^\circ = 6 \Delta_f H^\circ(\text{CO}_2) + 3 \Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_f H^\circ(\text{C}_6\text{H}_6) - \frac{15}{2} \Delta_f H^\circ(\text{O}_2)$$

$$(2) \quad \Delta_r H^\circ + \Delta_f H^\circ(\text{C}_6\text{H}_6) = 6 \Delta_f H^\circ(\text{CO}_2) + 3 \Delta_f H^\circ(\text{H}_2\text{O}) - \frac{15}{2} \Delta_f H^\circ(\text{O}_2)$$

$$(3) \quad \Delta_f H^\circ(\text{C}_6\text{H}_6) = 6 \Delta_f H^\circ(\text{CO}_2) + 3 \Delta_f H^\circ(\text{H}_2\text{O}) - \frac{15}{2} \Delta_f H^\circ(\text{O}_2) - \Delta_r H^\circ$$

[Return to Question 5 \(see page 39\)](#)

2.2.6 SOLUTION 6: HYDROGEN-ATOM SPECTROSCOPY

$$(1) \quad \bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2) \quad \bar{\nu} = \frac{R_H}{n_1^2} - \frac{R_H}{n_2^2} \quad (3) \quad \bar{\nu} + \frac{R_H}{n_2^2} = \frac{R_H}{n_1^2} \quad (4) \quad \frac{R_H}{n_2^2} = \frac{R_H}{n_1^2} - \bar{\nu}$$

$$(5) \quad \frac{R_H}{n_2^2} = \frac{R_H - n_1^2 \bar{\nu}}{n_1^2} \quad (6) \quad \frac{1}{n_2^2} = \frac{R_H - n_1^2 \bar{\nu}}{R_H n_1^2} \quad (7) \quad n_2^2 = \frac{R_H n_1^2}{R_H - n_1^2 \bar{\nu}} \quad (8) \quad n_2 = n_1 \sqrt{\frac{R_H}{R_H - n_1^2 \bar{\nu}}}$$

Rearranging the Rydberg equation (1) to obtain n_2 as the subject of the equation is a bit more difficult than it may appear at first sight. Expand out the bracket (2) on the right. (3) Take R_H/n_2^2 over to the left and then move $\bar{\nu}$ over to the right, gives (4). (5) Bring the right hand side to a common denominator of n_1^2 this is a crucial step as otherwise you cannot later take reciprocals. (6) Divide left and right by R_H . (7) Take reciprocals on both sides and (8) take the square root of both sides. In the last step of square rooting, the n_1 in the *numerator* of (7) can be square rooted and taken outside the square root bracket. On the other hand n_1 in the denominator of (7) *cannot* be square rooted because of the minus sign, the denominator is made up of two terms which must both be treated equally.

[Return to Question 6 \(see page 40\)](#)

2.2.7 SOLUTION 7: CHEMICAL EQUILIBRIUM AND CONCENTRATION CALCULATIONS

$$(1) K_c = \frac{[2x]^2}{[2-x][2-x]} = 55.64 \quad (2) \frac{[2x]^2}{[2-x]^2} = 55.64$$

$$(3) \frac{[2x]}{[2-x]} = \pm 7.4592 \quad (4) [2x] = \pm 7.4592 \times [2-x]$$

(1) Note that the $[HI]$ is *all* squared $[2x]^2$ it is *not* $2x^2$. The equilibrium constant equation is solved most easily by (2) writing the denominator as a square term and then in (3) take the square root of both sides and note the ± 7.4592 . (4) Move $[2-x]$ to the right.

$$(5) [2x] = \overset{+}{+7.4592 \times [2-x]} \quad (6) [2x] = \overset{-}{-7.4592 \times [2-x]}$$

$$(7) 2x = 14.9184 - 7.4592x \quad (8) 2x = -14.9184 + 7.4592x$$

$$(9) 9.4592x = 14.9184 \quad (10) 5.4592x = 14.9184$$

$$(11) x = 1.5771 \quad (12) x = 2.7327$$

The equations (5), (7), (9), and (11) carry out the algebra for the $+7.4592$ square root. The equations (6), (8), (10), and (12) process the -7.4592 square root. The concentrations of H_2 and I_2 which equal $[2-x]$ must be positive as you cannot have negative concentrations, so the chemically sensible root is $x = 1.5571$. The equilibrium concentrations are calculated by substituting $x = 1.5571$ as below.

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$$\begin{aligned}c_{\text{H}_2} &= [\text{H}_2] \text{ mol L}^{-1} = [2-x] \text{ mol L}^{-1} = 0.4429 \text{ mol L}^{-1} \\c_{\text{I}_2} &= [\text{I}_2] \text{ mol L}^{-1} = [2-x] \text{ mol L}^{-1} = 0.4429 \text{ mol L}^{-1} \\c_{\text{HI}} &= [\text{HI}] \text{ mol L}^{-1} = [2x] \text{ mol L}^{-1} = 3.1142 \text{ mol L}^{-1}\end{aligned}$$

[Return to Question 7 \(see page 21\)](#)

2.2.8 SOLUTION 8: CRYSTAL STRUCTURES BY X-RAY DIFFRACTION

$$\begin{aligned}(1) \quad 2d \sin \theta &= n\lambda & (2) \quad d &= \frac{n\lambda}{2 \sin \theta} & (3) \quad d &= \frac{1 \times 0.154 \text{ nm}}{2 \sin(11^\circ)} \\(4) \quad d &= \frac{1 \times 0.154 \text{ nm}}{2 \times 0.191} & (5) \quad d &= 0.403 \text{ nm}\end{aligned}$$

The Bragg equation (1) is rearranged so that d is the subject (2) and then substitute in the values of the variables (3). (4) Note that we do not need to change the units to the base unit of 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 (5).

[Return to Question 8 \(see page 42\)](#)

2.2.9 SOLUTION 9: POLYMER CHEMISTRY

$$\begin{aligned}(1) \quad \langle r \rangle^2 &= N l^2 \frac{1 - \cos \theta}{1 + \cos \theta} & (2) \quad \langle r \rangle^2 &= (5 \times 10^3)(154 \text{ pm})^2 \frac{1 - \cos(109.5^\circ)}{1 + \cos(109.5^\circ)} \\(3) \quad \langle r \rangle^2 &= 2.3741 \times 10^8 \text{ pm}^2 & (4) \quad \langle r \rangle &= \pm 1.5408 \times 10^4 \text{ pm}\end{aligned}$$

The average end-to-end distance equation (1) has the physical quantities substituted (2) for the variable symbols. It was not necessary to convert to metres, *but* it was necessary to have the units of the length in the equation. Clearly when we take the square root of (3) it is only the positive distance in (4) that is chemically sensible. The average end-to-end distance of the polymer $\langle r \rangle = 1.5408 \times 10^4 \text{ pm}$ which is about 2% of the stretched out “linear” length of polymer $77 \times 10^4 \text{ pm}$. Macromolecules both natural (*e.g.* DNA, RNA, proteins, and carbohydrates) and synthetic polymers will be covered in detail in your chemistry lectures.

[Return to Question 9 \(see page 43\)](#)

2.2.10 SOLUTION 10: CONJUGATED MOLECULES AND QUANTUM MECHANICS

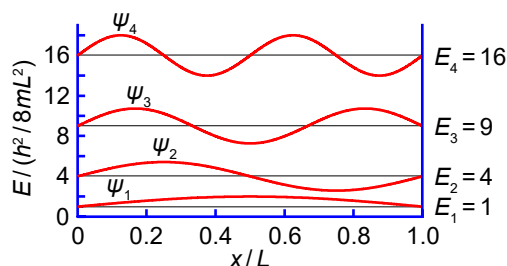


Figure 2.15: wavefunctions and energies for a particle in a one-dimensional box.

The wavefunctions for the π -electrons (Fig. 2.15) have to be zero at both ends of the polyene molecule so that the wavefunctions are “standing waves” which persists through time, these are called the “boundary conditions” in quantum mechanics. Another way of looking at the boundary conditions is that in order for the π -electrons to be confined within the polyene the wavefunctions must be zero at the two ends of the polyene.

$$\begin{aligned}
 (1) \quad \psi(x) &= A \cos(kx) + B \sin(kx) & (2) \quad \psi(0) = 0 \rightarrow A = 0 & (3) \quad \psi(x) = B \sin(kx) \\
 (4) \quad \psi(L) = 0 &\rightarrow \sin(kL) = \sin(n\pi x) & (5) \quad k = \frac{n\pi x}{L} & (6) \quad \psi(x) = B \sin\left(\frac{n\pi x}{L}\right)
 \end{aligned}$$

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The general wave equation (1) needs to fit with the two boundary conditions. (2) The left hand boundary condition $x = 0$ and $\psi(0) = 0$ but in radians $\cos(0) = 1$ and $\sin(0) = 0$. So the sine function agrees with the quantum mechanics but the cosine does not agree. Hence in order to remove the cosine term from the general wave equation we must set $A = 0$ to give (3). (4) The right hand boundary condition of the polyene molecule $x = L$ and $\psi(L) = 0$ and so in radians $\sin(kL)$ must be equal to zero. This means kL (in radians) must be equal an integral number $n = 1, 2, 3, \dots$ of π so $kL = n\pi$. The integer is a quantum number and in general quantization arises because of the fulfilling of boundary conditions such as the ones in this question. (5) Rearranging $kL = n\pi$ gives the value of the constant $k = n\pi/L$. (6) Finally we have the (incomplete) wavefunction for the particles, the π -electrons, in a one-dimensional box, the polyene conjugated molecule. The only constant that is yet to be found is B the normalization constant. The value of the constant B is calculated later in section 8.2.2.

[Return to Question 10 \(see page 44\)](#)

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 O–H distance is 0.9687 \AA and the half the H–H distance is 0.76955 \AA with θ the half angle for H–O–H.

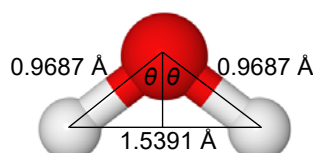


Figure 2.16: water O (red) and H (grey).

$$(1) \sin \theta = \frac{0.76955 \text{ \AA}}{0.9687 \text{ \AA}} = 0.79442 \quad (2) \theta = \sin^{-1}(0.79442) = 52.60^\circ \quad (3) \text{H}-\hat{\text{O}}-\text{H} = 105.2^\circ$$

(1) The distance multiple of 10^{-10} m is called an ångstrom with the symbol \AA , it is a common and convenient unit used by chemists as it is of the order of bond distances and atomic radii. (2) As θ is only half of the water bond angle, the calculated bond angle (3) is 105.2° close to but not equal to the tetrahedral angle 109.47° .

[Jump to Question 11 \(see page 45\)](#)

2.2.12 SOLUTION 12: WEAK ACIDS

$$\begin{aligned}
 (1) \quad 1.7539 \times 10^{-5} &= \frac{x^2}{0.15 - x} & (2) \quad (1.7539 \times 10^{-5})(0.15 - x) &= x^2 \\
 (3) \quad (2.6309 \times 10^{-6}) - (1.7539 \times 10^{-5}x) &= x^2 & (4) \quad x^2 + 1.7539 \times 10^{-5}x - 2.6309 \times 10^{-6} &= 0
 \end{aligned}$$

(1) The fraction x of acid lost in going to the equilibrium is given by this quadratic equation. (2) Rearrange the equation by moving $(0.15 - x)$ to the left hand side. (3) Multiply out the brackets. (4) Write the quadratic in the standard form.

$$\begin{aligned}
 (5) \quad x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\
 (6) \quad x &= \frac{-1.7539 \times 10^{-5} \pm \sqrt{(1.7539 \times 10^{-5})^2 - 4 \times 1 \times (-2.6309 \times 10^{-6})}}{2 \times 1} \\
 (7) \quad x &= \frac{-1.7539 \times 10^{-5} \pm \sqrt{3.0762 \times 10^{-10} + 1.0524 \times 10^{-5}}}{2}
 \end{aligned}$$

(5) The quadratic formula where the symbols have their conventional meanings. (6) Substitute our quadratic equation coefficients. (7) Note the change of sign to the second term within the square root and also the very large difference in magnitude between b^2 and $4ac$ terms.

$$\begin{aligned}
 (8) \quad x &= \frac{-1.7539 \times 10^{-5} \pm \sqrt{1.052430762 \times 10^{-5}}}{2} \\
 (9) \quad x &= \frac{-1.7539 \times 10^{-5} \pm 3.2441 \times 10^{-3}}{2} \\
 (10) \quad x &= 1.6133 \times 10^{-3} \quad (11) \quad x = -1.6308 \times 10^{-3}
 \end{aligned}$$

(8) 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 $4ac$. (9) 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 x is the *fraction* of acetic acid that has dissociated. A fraction is a *positive* number of less than one (unity). Another way of looking at this is that you cannot have a negative concentration, thus the chemically correct result is (10) that is, the concentration of hydronium ions in the acetic acid dissociation.

$$c_{\text{H}_3\text{O}^+} = x \text{ mol L}^{-1} = 1.6133 \times 10^{-3} \text{ mol L}^{-1}$$

Although not part of the question, this concentration of H_3O^+ has a $\text{pH} = -\log(1.6133 \times 10^{-3}) = 2.792$ which is acidic, as expected.

[Jump to Question 12 \(see page 45\)](#)

2.2.13 SOLUTION 13: THE SYNTHESIS OF AMMONIA

$$(1) \frac{[2x]^2}{[1-x][3-3x]^3} = 1.64 \times 10^{-4} \quad (2) \frac{4x^2}{[1-x]^3[1-x]^3} = 1.64 \times 10^{-4} \quad (3) \frac{x^2}{[1-x]^4} = 1.1070 \times 10^{-3}$$

$$(4) \frac{x}{[1-x]^2} = \sqrt{1.1070 \times 10^{-3}} \quad (5) \frac{x}{[1-x]^2} = 3.3272 \times 10^{-2} \quad (6) x = g(1-2x+x^2)$$

The solution to this problem is long but the solution is *not* difficult and working with pressures in bar rather than pascals simplifies the arithmetic. The equilibrium equation (1) may be solved for x by (2) taking out the numeral factors. (3) The numerical factors are taken over to the right and evaluated. (4) Square root both sides of the equation to give (5). (6) In order not to get lost it helps to keep the quadratic equation looking simple, let $g = 3.3272 \times 10^{-2}$ and take the denominator of (5) to the right and side and expand out $(1-x)^2$.

$$(7) x = g - 2gx + gx^2 \quad (8) gx^2 - (2g+1)x + g = 0$$

$$(9) x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (10) x = \frac{(2g+1) \pm \sqrt{(2g+1)^2 - 4g^2}}{2g}$$

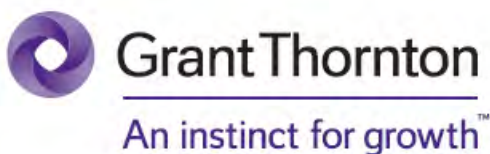
$$(11) x = \frac{(2g+1) \pm \sqrt{4g+1}}{2g} \quad (12) x = \frac{(2 \times 3.3272 \times 10^{-2} + 1) \pm \sqrt{4 \times 3.3272 \times 10^{-2} + 1}}{2 \times 3.3272 \times 10^{-2}}$$

$$(13) x = 32.025 \quad x = 0.031$$

DON'T EAT YELLOW SNOW

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Multiply out the bracket of (6) and rearrange to (7) and then into the standard quadratic form (8). The quadratic formula (9) has our variables substituted to give (10). (11) Square the term in the square root bracket and cancel out $4g^2$. (12) Substitute for $g = 3.3272 \times 10^{-2}$ and calculate the two roots (13) of the quadratic equation. As the mole *fraction* must be positive and less than unity then $x = 0.031$ is the chemically sensible result. This gives the three equilibrium partial pressures.

$$p_{\text{N}_2} = 1 - x = (1 - 0.031) \text{ bar} = 0.969 \text{ bar}$$

$$p_{\text{H}_2} = 3 - 3x = (3 - 3 \times 0.031) \text{ bar} = 2.907 \text{ bar}$$

$$p_{\text{NH}_3} = 2x = (2 \times 0.031) \text{ bar} = 0.062 \text{ bar}$$

[Return to Question 13 \(see page 47\)](#)

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 about logs, exponentials, and acid-base equilibrium.

3.1.1 DEFINITION OF A LOGARITHM

We are familiar with expressing a number as a power (also called an exponent) of a base number. These numbers may also be written as logarithms, the log is the power required to produce a given number.

- | | |
|-------------------------|---------------------------------|
| (1) $10^2 = 100$ | (2) $\log_{10}(100) = 2$ |
| (3) $5^3 = 125$ | (4) $\log_5(125) = 3$ |
| (5) $10^9 = 1000000000$ | (6) $\log_{10}(1000000000) = 9$ |
| (7) $2^8 = 256$ | (8) $\log_2(256) = 8$ |

(1) $10^2 = 100$ where “2” is the power and “10” is the base number and writing it as a log is equation (2). A second example (3) $5^3 = 125$ with “3” the power and “5” is the base number and (4) is written as a log. A third example (5) is $10^9 = 1000000000$ which is a billion with “9” the power and “10” the base number and (6) its log equivalent. A final example (7) is that of the byte a sequence of eight bits of information $2^8 = 256$ which is the standard for computer architectures and (8) its log. Logarithms (logs for short) are the inverse process to exponentiation.

The log base must be $b > 1$ if $b_c = a$ then $c = \log_b(a)$
pronounced "c is the log of a to base the b".

We can only take the log of a *pure number* but not of a physical quantity with units.
The number of *decimal* places of a log equals the number of *significant figures* of the number.

3.1.2 RULES OF LOGS

The rules of logs cover (1) the multiplication of the two numbers, (2) the division of the two numbers, and (3) the power of the number.

- (1) $\log_b(x \times y) = \log_b(x) + \log_b(y)$
 - (2) $\log_b\left(\frac{x}{y}\right) = \log_b(x) - \log_b(y)$
 - (3) $\log_b(x^n) = n \log_b(x)$
- Rules of logs

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3.1.3 ADDITIONAL RULES

$$\begin{aligned} (1) \log_b(b) &= 1 & (2) \log_b(b)^x &= x \\ (3) b^{\log_b(x)} &= x & (4) \log_b(a) &= \frac{1}{\log_a(b)} \end{aligned}$$

Additional rules of logs

The additional rules of logs are just special cases of the general rules above, (1) the number is the same as the base, (2) the number is the same as the base raised to a power, (3) the log is an exponent of the base number, and (4) when the number and the base are exchanged.

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 pronounced as “logs” or “common logs”. Large numbers have positive powers *e.g.* 10^{23} with $\log(1 \times 10^{23}) = 23$, and very small numbers have negative powers *e.g.* 10^{-34} with $\log(1 \times 10^{-34}) = -34$. An example is pH which range from 0 to 14, from a high concentration of protons $\text{pH} = 0$ or $[\text{H}^+] = 10^0 = 1 \text{ mol L}^{-1}$ to the very low concentration of $\text{pH} = 14$ or $[\text{H}^+] = 1 \times 10^{-14} \text{ mol L}^{-1}$.

Logs to base “e” are normally written as “ln” rather than \log_e and they are pronounced as “natural logs” or “Napierian logs” after John Napier (1550–1617) a Scot from Edinburgh who invented logs and popularized the modern usage of the decimal point in writing numbers. Natural logs are important for their maths properties which model many natural phenomena, hence they appear often in science and engineering. The base number of natural logs is Euler’s number “e” which comes from the infinite series below and is named after the Swiss mathematician Leonard Euler (pronounced as “oiler” in English). Euler’s number is easy to remember to 16 significant figures (if you like that sort of thing), it is 2.7 followed by 1828 twice then 45, 90, 45 the angles of a right-angled isosceles triangle $e = 2.718281828459045\dots$ after which it is really boring. Below are two alternative ways of defining Euler’s number (truncated at small values of n).

$$\begin{aligned} e &= \lim_{n \rightarrow \infty} \left(1 + \frac{1}{n}\right)^n = \overbrace{1}^{n=0} \overbrace{2}^{n=1} \overbrace{2.25}^{n=2} \overbrace{2.488}^{n=5} \overbrace{2.593}^{n=10} \overbrace{2.704}^{n=100} \overbrace{2.716}^{n=1000} \overbrace{2.718}^{n=10000} \overbrace{\dots}^{n=\dots} \\ e &= \sum_{n=0}^{\infty} \frac{1}{n!} = \frac{1}{0!} + \frac{1}{1!} + \frac{1}{1!} + \frac{1}{3!} + \frac{1}{4!} + \frac{1}{5!} + \frac{1}{6!} + \frac{1}{7!} + \frac{1}{8!} + \frac{1}{9!} + \frac{1}{10!} + \dots \approx 2.718 \end{aligned}$$

Euler’s number

The $n = 0$ term of the first definition uses the fact that anything raised to the power 0 equals one. The second definition has the symbol “!” which means the factorial of the number (see section 1.2.9). Note that e is the symbol for a numerical constant it is *not* a variable and e is similar to π (also a symbol for a numerical constant) or any other number such as 10 is written in upright roman script not in italic script. In science and engineering we quite often find equations with e^x or e^{-x} in them. The negative power is just a special case of e^x in which the sign is positive or negative for even and odd power of x , respectively.

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

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

Euler's number raised to the powers x and $-x$

The equation $y = e^x$ may also be written as $y = \exp(x)$ with “exp” *all lower case*. This exp notation is used for greater clarity particularly in printed material. For example the Arrhenius equation $k = A e^{-E_a/RT}$ can also be written as $k = A \exp(-E_a/RT)$. However, be careful in using some calculators with a key marked EXP, *all capitals*, which means “10 raised to an exponent”, where you type in the power (the exponent).

$$(1) \log_b(a) = \frac{\log_b(x)}{\log_b(x)} \quad (2) \log_e(10) = \frac{\log_e(x)}{\log_{10}(x)} \quad (3) 2.3026 = \frac{\ln(x)}{\log(x)}$$

Change of log base



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An important and common process is to *change the base* of the logs. (1) Shows the general formula for changing from base number (*b*) to base number (*a*). (2) The specific change between natural logs and base-10 logs and in (3) this change is written in the conventional way.

3.1.5 INDICIAL EQUATIONS

The equation $12^{2x} = 35.4$ is an example of an indicial equation, the variable is present as an index (or exponent or power). To solve (1) for x , we take logs on both sides (2), from the rules of logs we can take the power down (3), and evaluate the logs in (4). The solution of the indicial equation is (5).

$$\begin{array}{llll} (1) & 12^{2x} = 35.4 & (2) & \log(12^{2x}) = \log(35.4) \\ (3) & 2x \times \log(12) = \log(35.4) & (4) & 2x \times 1.07918 = 1.54900 \\ (5) & x = 0.71768 \end{array}$$

3.1.6 ACID-BASE EQUILIBRIUM

The concentrations of protons H^+ (present as hydronium H_3O^+ ions) and hydroxyl ions OH^- are very small in aqueous solution and involve many *negative* powers of ten in mol L^{-1} .

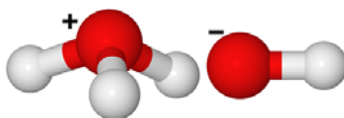
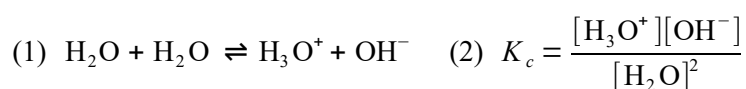


Figure 3.1: hydronium and hydroxyl ions.

Humans are normally happier dealing with positive numbers that are in the range of 0-100. The “p” part of the variables pH and pOH refers to the power (index or exponent) of these small concentrations which are made more manageable by using logarithms. Taking the negative of the log converts the negative number into a positive number. The symbols pH and pOH are by convention written with upright roman script not as italics.

$$\text{pH} \approx -\log_{10} \left[\frac{c(H^+)}{\text{mol L}^{-1}} \right] \quad \text{pOH} \approx -\log_{10} \left[\frac{c(OH^-)}{\text{mol L}^{-1}} \right] \quad \text{Definitions: pH and pOH}$$

Strictly speaking pH and pOH should be defined in terms of the “thermodynamic activity a ” of H^+ and OH^- but for most purposes concentrations are of adequate precision.



The self-ionization or autoprotolysis of water (1) has an equilibrium constant K_c (2) but as the concentration of the solvent water is to a very good approximation constant, we may combine the water concentration with the equilibrium constant $[\text{H}_2\text{O}]^2 \times K_c = K_w$ the autoprotolysis (or self-ionization) constant of water.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \text{Definition: autoprotolysis constant water}$$

At 25°C, $K_w = 1.0 \times 10^{-14}$ (K_w is temperature dependent). We define $\text{p}K_w$ in a similar fashion to pH and pOH.

$$\text{p}K_w = -\log_{10}(K_w) \quad \text{p}K_w = \text{pH} + \text{pOH} = 14 \quad \text{Definition: p}K_w$$

$$(3) \quad \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \quad (4) \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$(5) \quad \text{p}K_a = -\log_{10}(K_a) \quad (6) \quad \text{p}K_a = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

For an acid (3) we can define an acid dissociation constant (4) K_a again incorporating the approximately constant solvent concentration $[\text{H}_2\text{O}]$ into K_a . The $\text{p}K_a$ of the acid dissociation constant is defined (5) in a familiar way. The $\text{p}K_a$ is related (6) to the pH from equation (4). Rearranging the last equation (6) we obtain the Henderson-Hasselbalch equation which applies to weak acids and buffer solutions.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad \text{Henderson-Hasselbalch equation}$$

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 $1.04 \times 10^{-5} \text{ mol L}^{-1}$. Calculate the pOH and then the pH of the solution.

[Jump to Solution 1 \(see page 71\)](#)

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 hydronium ions for which human life can be sustained?

[Jump to Solution 2 \(see page 71\)](#)

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 consists of 0.027 mol L^{-1} of aqueous NH_3 ($[\text{A}^-] = 0.027 \text{ mol L}^{-1}$) and 0.025 mol L^{-1} of NH_4Cl for which ammonium chloride has a $\text{p}K_{\text{a}} = 9.25$. The ionic salt NH_4Cl is fully dissociated into NH_4^+ and Cl^- and the ammonium ion NH_4^+ is a weak acid and so $[\text{HA}] = 0.025 \text{ mol L}^{-1}$.

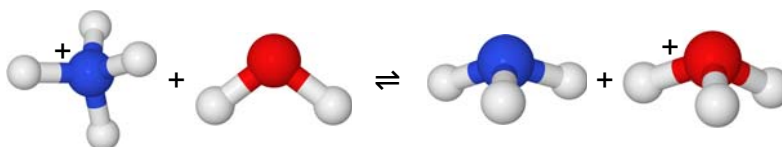
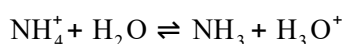


Figure 3.2: ammonium ion, water, ammonia, and hydronium ion.

[Jump to Solution 3 \(see page 72\)](#)

3.2.4 QUESTION 4 FIRST-ORDER KINETICS

The concentration of the reactant, say A , 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.

$$[A] = [A]_0 \exp(-kt) \quad \text{First-order rate law}$$

Where $[A]_0$ is the initial concentration of the reactant at time $t = 0$, $[A]$ is the concentration of the reactant at a later time t , and k is the rate constant for this particular reaction taking place at constant temperature. Sketch the *shape* of the graph of $[A]/[A]_0$ plotted as the y -axis against kt plotted as the x -axis (k is constant at a given temperature) and label the two axes. You do *not* need to calculate anything. As a hint Fig. 3.3 is a plot of the negative exponential curve $y = \exp(-x)$. The negative exponential has an intercept at $(0, 1)$ and has two asymptotes shown in Fig. 3.3 where the arrows mean “in the limit”.

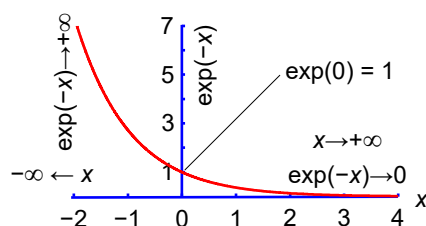


Figure 3.3: a negative exponential curve.

[Jump to Solution 4 \(see page 72\)](#)

3.2.5 QUESTION 5: FIRST-ORDER KINETICS

For a first-order rate law reaction write the natural log form of the rate law with $\ln([A]/[A]_0)$ as the subject.

[Jump to Solution 5 \(see page 73\)](#)

3.2.6 QUESTION 6: FIRST-ORDER KINETICS

For a first-order rate law reaction sketch three possible graphs that give straight line plots for the rate law. Label the axes and give the meanings of the gradient and intercept. Comment on which is the best of these three graphs.

[Jump to Solution 6 \(see page 73\)](#)

3.2.7 QUESTION 7: FIRST-ORDER KINETICS

If a first-order reaction has a rate constant, $k = 1.83 \times 10^{-4} \text{ s}^{-1}$, calculate how long it would take for the concentration of reactant $[A]$ to decrease from $3.25 \times 10^{-3} \text{ mol L}^{-1}$ to $2.18 \times 10^{-3} \text{ mol L}^{-1}$.

[Jump to Solution 7 \(see page 74\)](#)

3.2.8 QUESTION 8: THE ARRHENIUS EQUATION

So far we have looked at the rate law which shows the variation of the rate of reaction v with concentration and time, under constant temperature conditions. However, the rate constant k of a chemical reaction increases with the absolute temperature T , this is modelled by the Arrhenius equation.

$$k = A \exp\left(-\frac{E_a}{RT}\right) \text{ Arrhenius equation}$$

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

[Jump to Solution 8 \(see page 74\)](#)

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3.2.9 QUESTION 9: THE ARRHENIUS EQUATION

Write the Arrhenius equation in the form of natural logs. Sketch the straight line graph with the axes labelled for the Arrhenius equation. Give the meanings of the gradient and intercept in terms of the Arrhenius equation.

[Jump to Solution 9 \(see page 75\)](#)

3.2.10 QUESTION 10: THE ARRHENIUS EQUATION

On your graph for Question 9, sketch the results for a linear plot for two different chemical reactions, one with a large activation energy and the other with a small activation energy, clearly label the two lines. Assume that both chemical reactions have the same value for the pre-exponential factor A .

[Jump to Solution 10 \(see page 76\)](#)

3.2.11 QUESTION 11: THE ARRHENIUS EQUATION

The activation energy for the decomposition of hydrogen peroxide on a platinum catalyst is $E_a = 48.9 \text{ kJ mol}^{-1}$ and $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$.

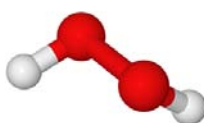
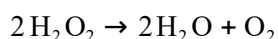


Figure 3.4: hydrogen peroxide,
oxygen (red) and hydrogen (light grey).

The effect of increasing the temperature is shown by calculating the ratio of the rate constant k_2 at 30°C to the rate constant k_1 at 20°C .

[Jump to Solution 11 \(see page 77\)](#)

3.2.12 QUESTION 12: THE NERNST EQUATION

The following redox chemical reaction (redox is short for reduction-oxidation) can be made into an electrochemical cell to derive electrical energy, Fig. 3.5. The cell is called the Daniell cell and has a voltage difference between the zinc and copper metal electrodes which is given by the Nernst equation. This voltage difference drives electrons through an external circuit. The zinc sulfate and copper sulfate solutions are separated by a porous barrier which allows the ions to pass through.

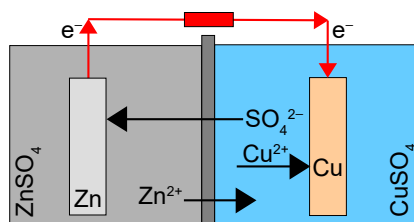
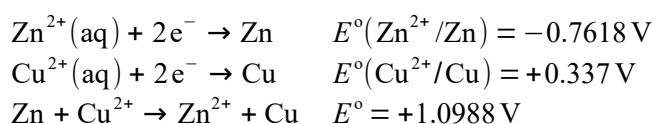


Figure 3.5: schematic diagram of a Daniell cell with a porous barrier.



The standard electrode potentials E° are with solutions of 1 mol L^{-1} and 298.15 K . The cell potential E varies with the temperature of the cell and the concentrations and is given by the Nernst equation.

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Nernst equation for the Daniell cell

Where n is the number of electrons transferred in the stoichiometric reaction (in this case $n = 2$), R is the gas constant, T the temperature in kelvins, and F is the Faraday constant (one mole of elementary charge).

$$F = e N_{\text{A}} = 96485 \text{ C mol}^{-1}$$

Faraday constant

Calculate the concentration of zinc ions $[\text{Zn}^{2+}]$ for $E = 1.21 \text{ V}$, $[\text{Cu}^{2+}] = 0.1 \text{ mol L}^{-1}$, $T = 298.15 \text{ K}$ and $E^{\circ} = 1.10 \text{ V}$. Make use of the conversion $1 \text{ joule} = 1 \text{ coulomb volt}$ ($1 \text{ J} = 1 \text{ C V}$).

[Jump to Solution 12 \(see page 78\)](#)

3.2.13 QUESTION 13: CHEMICAL WORK AT CONSTANT PRESSURE

$$\Delta_r G^\circ = -RT \ln K_c^\circ \quad \text{Standard Gibbs energy of reaction}$$

The standard Gibbs energy of reaction $\Delta_r G^\circ$ is the maximum non-expansion work that a chemical reaction can supply at constant temperature and pressure, K_c° is the equilibrium constant. Calculate $\Delta_r G^\circ$ with appropriate error limits, for a reaction which has an equilibrium constant $K_c^\circ = 1.8 \times 10^{-5}$ at $T = 298.15$ K and $R = 8.3145$ J K⁻¹ mol⁻¹ is the gas constant.

[Jump to Solution 13 \(see page 79\)](#)

3.2.14 QUESTION 14: RADIOACTIVE DECAY

Radioactive decay is a first-order chemical reaction which has an exponential decay in the reactant concentration, the radioactive element. Starting with an original number of radioactive atoms n_0 at time zero, the number of radioactive atoms n left after a certain time t is given below, where k is the rate constant for this decay reaction.

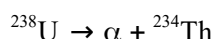
$$n = n_0 \exp(-kt) \quad \text{First-order radioactive decay}$$

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The decay of ^{238}U has a half-life of 4.4683×10^9 years which is close to the age of the earth 4.54 ± 0.05 billion years (4.54×10^9 years $\pm 1\%$). As the name implies the half-life is the time for n/n_0 to equal 0.5. Uranium-238 decays predominantly to thorium-234 by an alpha particle decay mechanism, where an alpha particle (α) is a fast moving helium-4 nucleus $^4\text{He}^{2+}$. Calculate the rate constant for this uranium-238 decay process.



[Jump to Solution 14 \(see page 79\)](#)

3.3 WEEK 3 TUTORIAL SOLUTIONS

3.3.1 SOLUTION 1: ACID-BASE EQUILIBRIUM

$$\begin{array}{ll} (1) [\text{OH}^-] = 1.04 \times 10^{-5} \text{ mol L}^{-1} & (2) \text{pOH} = -\log_{10}(1.04 \times 10^{-5}) = 4.98 \\ (3) \text{pH} + \text{pOH} = 14.00 & (4) \text{pH} = 14.00 - 4.98 = 9.02 \end{array}$$

An alkaline solution.

[Return to Question 1 \(see page 64\)](#)

3.3.2 SOLUTION 2: ACID-BASE EQUILIBRIUM

From the definition of a logarithm we have $[\text{H}_3\text{O}^+] = 10^{-7.8}$. 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” which equals 10^x not “shift-ln” which equals e^x . Human blood covers only a small range of hydronium ion concentrations as shown below.

$$\begin{array}{llll} (1) \text{pH}_{\text{max}} = 7.8 & (2) 7.8 = -\log_{10}[\text{H}_3\text{O}^+]_{\text{max}} & (3) [\text{H}_3\text{O}^+]_{\text{max}} = 10^{-7.8} = 1.58 \times 10^{-8} \text{ mol L}^{-1} \\ (4) \text{pH}_{\text{min}} = 7.0 & (5) 7.0 = -\log_{10}[\text{H}_3\text{O}^+]_{\text{min}} & (6) [\text{H}_3\text{O}^+]_{\text{min}} = 10^{-7.0} = 1.00 \times 10^{-7} \text{ mol L}^{-1} \end{array}$$

[Return to Question 2 \(see page 64\)](#)

3.3.3 SOLUTION 3: ACID-BASE EQUILIBRIUM

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]} \quad \text{pH} = 9.25 + \log_{10} \frac{0.027 \text{ mol L}^{-1}}{0.025 \text{ mol L}^{-1}} \quad \text{pH} = 9.28$$

This alkaline buffer has a pH of 9.28. When using your calculator make sure that you use brackets, type $\log(0.027/0.025) = 0.03342$ and *don't* type $\log 0.027/0.025$ which may “incorrectly” give -62.745 .

[Return to Question 3 \(see page 65\)](#)

3.3.4 SOLUTION 4: FIRST-ORDER KINETICS

$$[\text{A}] = [\text{A}]_0 \exp(-kt) \quad \frac{[\text{A}]}{[\text{A}]_0} = \exp(-kt)$$

Remember that the rate constant k is constant for a given reaction at a fixed temperature and plotting $[\text{A}]/[\text{A}]_0$ versus kt is a negative exponential (Fig. 3.6). The ratio $[\text{A}]/[\text{A}]_0$ is a dimensionless variable as is kt for a first-order reaction. The reaction starts at time equals zero $kt = 0$ and there are no negative times for the reaction, the intercept at $kt = 0$ is $[\text{A}]/[\text{A}]_0 = 1$ that is $[\text{A}] = [\text{A}]_0$. Note that using this non-linear plot it is *not* easy to deduce the rate constant k , we will return to this later on. Fig. 3.6 shows that with an exponential decrease, that increasing numbers of half-lives the concentration of the reactant decreases by $1/2$ of the previous value each time. As the time tends towards infinity the concentration asymptotically approaches zero.

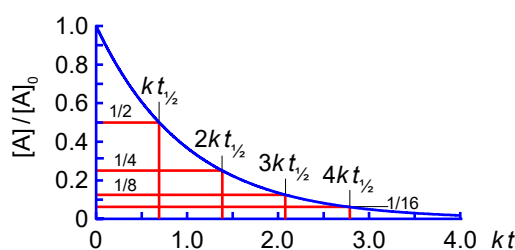


Figure 3.6: $[\text{A}] / [\text{A}]_0$ versus kt for a first-order reaction.

[Return to Question 4 \(see page 65\)](#)

3.3.5 SOLUTION 5: FIRST-ORDER KINETICS

$$(1) [A] = [A]_0 \exp(-kt) \quad (2) \ln[A] = \ln([A]_0 \exp(-kt)) \quad (3) \ln[A] = \ln[A]_0 + \ln(\exp(-kt))$$

$$(4) \ln[A] = \ln[A]_0 - kt \quad (5) \ln[A] - \ln[A]_0 = -kt \quad (6) \ln \frac{[A]}{[A]_0} = -kt$$

Starting with the first order kinetics equation (1), take natural logs (2) on both sides, expand out the right hand side of (2) into the sum of the log of each term (3). The natural log of the exponential in (3) is just the exponent $-kt$, (4). Move $\ln[A]_0$ to the left hand side (5) and convert the difference of two logs into the log of the ratio (6).

[Return to Question 5 \(see page 66\)](#)

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. Firstly, from section 3.3.5 we have the rate law in terms of a linear equation (Fig. 3.7 left). Secondly, from the rules of logs, section 3.1.2, we can invert the log on the left hand side of the above equation and the right hand side changes



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sign (Fig. 3.7 centre). Thirdly, in the intermediate stage section 3.3.5 equation (4) allows a third and equally valid straight line graph to be plotted (Fig. 3.7 right).

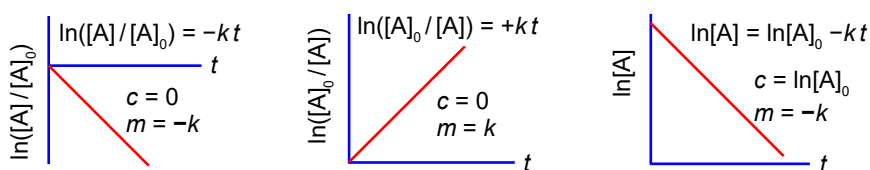


Figure 3.7: three possible first-order rate law linear plots.

This plot on the right has the advantage that you don't need to measure the value of $\ln[A]_0$ which you would for the other two plots and which may be difficult to experimentally accurately measure. Also with the plot on the right we are not plotting a log of a *ratio* which may show only small variations in $[A]/[A]_0$ (left) or very large variations in $[A]_0/[A]$ (middle) for small changes in $[A]$.

[Return to Question 6 \(see page 66\)](#)

3.3.7 SOLUTION 7: FIRST-ORDER KINETICS

We write the rate law as a log of a ratio and note that logs are dimensionless as they are a ratio of similar physical quantities, so the units cancel and we are taking the natural log of a pure number (as we *must* do).

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

$$\ln \frac{2.18 \times 10^{-3} \text{ mol L}^{-1}}{3.25 \times 10^{-3} \text{ mol L}^{-1}} = -1.83 \times 10^{-4} \text{ s}^{-1} t$$

$$-0.39933 = -1.83 \times 10^{-4} \text{ s}^{-1} t \quad t = 2182 \text{ s} = 36 \text{ m } 22 \text{ s}$$

[Return to Question 7 \(see page 66\)](#)

3.3.8 SOLUTION 8: THE ARRHENIUS EQUATION

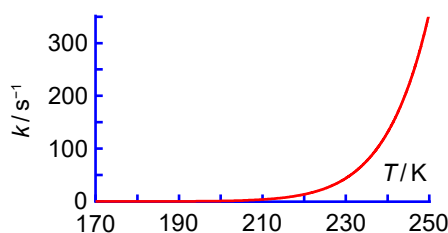


Figure 3.8: plot of k against T for first-order reaction data (smoothed data).

Fig. 3.8 shows the curved plot of the rate constant against the temperature which for clarity is with smoothed data (no random errors). This plot visually emphasizes the exponential nature of the rate constant's dependence upon temperature. Otherwise this plot is not very useful 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 as in section 3.3.9.

[Return to Question 8 \(see page 67\)](#)

3.3.9 SOLUTION 9: THE ARRHENIUS EQUATION

$$\begin{aligned}
 (1) \quad k &= A \exp\left(-\frac{E_a}{RT}\right) & (2) \quad \ln k &= \ln\left(A \exp\left(-\frac{E_a}{RT}\right)\right) \\
 (3) \quad \ln k &= \ln A + \ln\left(\exp\left(-\frac{E_a}{RT}\right)\right) & (4) \quad \ln k &= \ln A - \frac{E_a}{RT}
 \end{aligned}$$

We can go from the exponential form of the Arrhenius equation (1) to the log form by taking natural logs on both sides (2). The log on the right of (2) is a product of two terms which can be separated as the sum of two log terms (3) the second term is now the natural-log of an exponential, which is just equal to the exponent (4). Let us write the log form of the Arrhenius equation (4) with the $1/T$ term written explicitly, this helps us see that the log form of the Arrhenius equation is in the form of a straight line equation written as $y = c + mx$.

$$\underbrace{\ln k}_{y} = \underbrace{\ln A}_{c} + \underbrace{\left(-\frac{E_a}{R}\right)}_{m} \underbrace{\frac{1}{T}}_{x}$$

Log form of the Arrhenius equation

Plotting $\ln k$ as the y -axis and $1/T$ as the x -axis is called an “Arrhenius plot” the intercept $c = \ln A$ and the gradient $m = -E_a/R$.

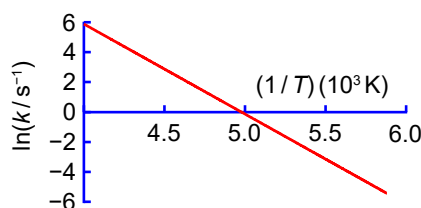


Figure 3.9: Arrhenius plot.

Fig. 3.9 uses the same smoothed data as Fig. 3.8. Notice a best straight line would end a long way from the y -axis intercept (the axes cross at $x = 4.0$ in this example). So drawing an extension to the best straight line is *not* the way forward as it will lead to *very* large errors. The equation of the best line was obtained using a spreadsheet is shown below.

$$\overbrace{\ln\left(\frac{k}{\text{s}^{-1}}\right)}^y = \overbrace{(29.9336)}^c \overbrace{(-6.01310 \times 10^3 \text{ K})}^{+m} \overbrace{\frac{1}{T}}^x$$

$$\begin{aligned} (5) \quad m &= \frac{y}{x} = \frac{\ln(k/\text{s}^{-1})}{(1/T)(10^3 \text{ K})} = -6.01310 & (6) \quad m &= \frac{\ln(k/\text{s}^{-1})}{1/T} = -6.01310 \times 10^3 \text{ K} \\ (7) \quad E_a &= -(-6.01310 \times 10^3 \text{ K})(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) & (8) \quad E_a &= 49992 \text{ J mol}^{-1} = 50 \text{ kJ mol}^{-1} \end{aligned}$$

The graphs axes are plotted as pure numbers (5). Logs are pure numbers, as in $\ln(k/\text{s}^{-1})$ and we cannot separate the units inside the log term. However, we *must* separate the units and multiplier of $1/T$ as the units (kelvin) and the multiplier are an integral part of the gradient m in (6). The gradient of the Arrhenius equation in log form is $m = -E_a/R$ and in (7) we calculate the activation energy by moving R over to the right. The activation energy in (8) is quoted in the conventional units of kJ mol^{-1} .

$$(9) \quad c = \ln(A/\text{s}^{-1}) = 29.9336 \quad (10) \quad A/\text{s}^{-1} = \exp(29.9336) \quad (11) \quad A = 1.0 \times 10^{13} \text{ s}^{-1}$$

The intercept occurs when $x = 0$ which is long way outside our plotted area, from the equation of the best-fit straight line $c = \ln(A/\text{s}^{-1}) = 29.9336$ in (9). We antilog both sides in (10) *only then* are we allowed to take the units over to the right in (11) as it is no longer a log.

[Return to Question 9 \(see page 68\)](#)

3.3.10 SOLUTION 10: THE ARRHENIUS EQUATION

Fig. 3.10 shows that the reaction with the larger activation energy $E_a = 50 \text{ J mol}^{-1}$ is *more* affected by changes in temperature (steeper gradient) than the one with a smaller activation energy $E_a = 20 \text{ J mol}^{-1}$. In the limiting case of zero activation energy the rate constant would be independent of temperature! Both plots in Fig. 3.10 have the same intercept $c = \ln(k/\text{s}^{-1}) = \ln(A/\text{s}^{-1}) = 29.9336$ which as we have seen gives $A = \exp(29.9336) \text{ s}^{-1}$ and $A = 1.0 \times 10^{13} \text{ s}^{-1}$.

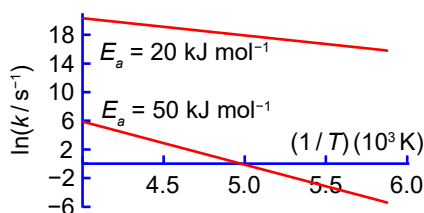


Figure 3.10: plot of $\ln k$ versus $1/T$ for high and low activation energies.

[Return to Question 10 \(see page 68\)](#)

3.3.11 SOLUTION 11: THE ARRHENIUS EQUATION

$$\begin{aligned}
 (1) \quad \ln k_1 &= \ln A - \frac{E_a}{RT_1} & (2) \quad \ln k_2 &= \ln A - \frac{E_a}{RT_2} & (3) \quad \ln \frac{k_2}{k_1} &= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} \\
 (4) \quad \ln \frac{k_2}{k_1} &= -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) & (5) \quad \ln \frac{k_2}{k_1} &= -\frac{48.9 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{303.15 \text{ K}} - \frac{1}{293.15 \text{ K}} \right) \\
 (6) \quad \ln \frac{k_2}{k_1} &= 0.6618 & (7) \quad \frac{k_2}{k_1} &= \exp(0.6618) & (8) \quad \frac{k_2}{k_1} &= 1.9383
 \end{aligned}$$

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The increase in temperature from T_1 to T_2 for the Arrhenius equation is most easily handled using the log forms of the Arrhenius equation, (1) and (2). Subtracting the log equations and write the subtraction of the two log terms as the log of the ratio of the terms (3) and on subtraction the two $\ln(A)$ terms cancels out. The common factor $-E_a/R$ is taken out of the bracketed term in (4). Substitute the physical quantities in (5) for the variables gives (6). Take the antilog of (6) in (7) to obtain the ratio of rate constants in (8).

Note that the activation energy is quoted in kJ mol^{-1} but must be converted to the base unit of J mol^{-1} in order to cancel out the units, and also that the temperature T must *always* be in kelvin. 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 . This is *only* true for reactions with activation energies of about 50 kJ mol^{-1} .

[Return to Question 11 \(see page 68\)](#)

3.3.12 SOLUTION 12: THE NERNST EQUATION

$$\begin{array}{ll}
 (1) \quad E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} & (2) \quad \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{(E^\circ - E)nF}{RT} \\
 (3) \quad \ln \frac{[\text{Zn}^{2+}]}{0.1 \text{ mol L}^{-1}} = \frac{(-0.11 \text{ V})2(96485 \text{ J V}^{-1} \text{ mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} & (4) \quad \ln \frac{[\text{Zn}^{2+}]}{0.1 \text{ mol L}^{-1}} = -8.5627 \\
 (5) \quad [\text{Zn}^{2+}] = (1.9110 \times 10^{-4})(0.1 \text{ mol L}^{-1}) & (6) \quad [\text{Zn}^{2+}] = 1.9110 \times 10^{-5} \text{ mol L}^{-1}
 \end{array}$$

The Nernst equation for the $\text{Zn}^{2+}/\text{Cu}^{2+}$ redox reaction (1) is rearranged in (2) so that the log term containing $[\text{Zn}^{2+}]$ is the subject. Substitute for the variables in (3) gives (4). Take antilogs of (4) and then you are able to multiply by 0.1 mol L^{-1} on the right hand side of (5). The unknown zinc ion concentration (6) has been measured electrochemically.

Electrochemistry has given us power sources such as batteries and fuel cells. Electrochemical analysis is used in measuring the concentrations of metal ions in drinking water, rivers, lakes, off-shore water, blood, drinks, food products, and in environmental pollution monitoring. Electrochemistry is used in the industrial production of many important metals *e.g.* aluminium and magnesium, used in aircraft fuselages, laptop and camera cases, and thin-shell buildings in modern architectural designs.

[Return to Question 12 \(see page 69\)](#)

3.3.13 SOLUTION 13: CHEMICAL WORK AT CONSTANT PRESSURE

$$\begin{aligned} (1) \quad \Delta_r G^\circ &= -RT \ln K & (2) \quad \Delta_r G^\circ &= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(1.8 \times 10^{-5}) \\ (3) \quad \Delta_r G^\circ &= 2.7083 \times 10^4 \text{ J mol}^{-1} & (4) \quad \Delta_r G^\circ &= (27.08 \pm 0.14) \text{ kJ mol}^{-1} \end{aligned}$$

The equilibrium constant K° is only quoted to two significant figures and a variation in K° of $\pm 0.1 \times 10^{-5}$ gives $\Delta_r G^\circ$ with a precision of $\pm 14 \text{ J mol}^{-1}$. Results are normally quoted in multiples of 10^3 or 10^{-3} and with the appropriate multiple symbol. The precision and the value are quoted in brackets with both of them having the same units and multiple as in (4).

[Return to Question 13 \(see page 70\)](#)

3.3.14 SOLUTION 14: RADIOACTIVE DECAY

$$\begin{aligned} (1) \quad n &= n_0 \exp(-kt) & (2) \quad \frac{n}{n_0} &= \exp(-kt) & (3) \quad 0.5 &= \exp(-k t_{1/2}) \\ (4) \quad \ln(0.5) &= -k t_{1/2} & (5) \quad -0.69315 &= -k(4.4683 \times 10^9 \text{ year}) & (6) \quad k &= 1.5513 \times 10^{-10} \text{ year}^{-1} \end{aligned}$$

Clearly the natural decay rate constant of uranium-238 is very small ($k \approx 10^{-10} \text{ year}^{-1}$), indeed during the lifetime of the earth only about half of the uranium-238 originally present at its formation has been converted to thorium-234 which is itself unstable and decays further by fission reactions.

[Return to Question 14 \(see page 70\)](#)

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 a selected frequency ν is directed at a sodium metal target inside a vacuum system. Electrons are ejected from the sodium photocathode and a variable “stopping” voltage is applied to turn back all but those electrons with the highest kinetic energy. This is the maximum kinetic energy of the ejected electrons E_{KE} . The experiment consists of altering the frequency of the light and measuring the maximum kinetic energy of the ejected electrons, the photoelectrons.



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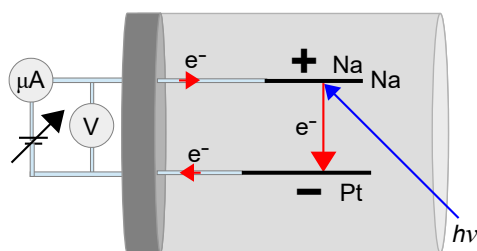


Figure 4.1: schematic of a photoelectric apparatus.

The UV photons must have a minimum frequency for them to eject any photoelectrons from the photocathode, the UV photon $h\nu$ is annihilated when it is absorbed. The minimum frequency corresponds to a minimum energy $h\nu$ of the photons, this minimum energy is called the “work function” of the metal Φ (upper case italic Greek phi) the work function is the solid-state equivalent to the ionization energy of a gas phase atom. Different metals, for example caesium, sodium, or potassium have different work functions.

$$h\nu = \Phi + E_{\text{KE}} \quad \text{Photoelectric effect}$$

A Heriot-Watt University student in the undergraduate chemistry lab experimentally measured the maximum kinetic energy of the photoelectrons as a function of the frequency of the light for a sodium photocathode.

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

Plot the graph of E_{KE} against the frequency ν either using a spreadsheet or manually (good practice for exams). Does the data form a straight line plot, *i.e.* is the maximum energy of the ejected electrons proportional to the frequency of the light hitting the sodium metal target? Determine the values of the gradient of the line which is Planck’s constant h . Determine the work function Φ from the x -axis intercept (*not* the y -axis intercept).

[Jump to Solution 1 \(see page 85\)](#)

4.1.2 QUESTION 2: PRESSURE-VOLUME EXPERIMENTAL DATA FOR CARBON DIOXIDE



Figure 4.2: carbon dioxide.

The volume of one mole of CO_2 gas was measured $V_{\text{m}}/\text{L mol}^{-1}$ as the pressure p/atm (atmospheres) was varied at a constant temperature of 313 K. The former unit of pressure was the atmosphere $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$ the standard pressure is $1 \text{ bar} = 1 \times 10^5 \text{ Pa (N m}^{-2}\text{)}$.

p/atm	1	10	50	100	200	500
$V_{\text{m}}/\text{L mol}^{-1}$	25.51	2.45	0.38	0.07	0.05	0.04

Either using a spreadsheet or manually plot: (1) p/atm versus $V_{\text{m}}/\text{L mol}^{-1}$, (2) $\log(p/\text{atm})$ against $\log(V_{\text{m}}/\text{L mol}^{-1})$ and (3) p/atm versus $(1/V_{\text{m}})(\text{L mol}^{-1})$ and comment upon each of the plots.

[Jump to Solution 2 \(see page 86\)](#)

4.1.3 QUESTION 3: EXPERIMENTAL ARRHENIUS PLOT

$$k = A \exp(-E_{\text{a}}/RT)$$

The Arrhenius equation was introduced in last week's questions. Firstly, using the following experimental data for the rate constants and temperatures of a kinetically first-order reaction



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draw a graph of $\ln(k/s^{-1})$ versus $(1/T)(10^3 \text{ K})$. 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
$k/(10^{-3} \text{ s}^{-1})$	5.26	7.56	14.4	22.7	48.3	62.1	119

[Jump to Solution 3 \(see page 87\)](#)

4.1.4 QUESTION 4: EXPERIMENTALLY DETERMINATION 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 of reaction* with respect to that compound. For example a particular chemical reaction involving H_2 has an experimental rate of the reaction is below.

$$v = k[\text{H}_2]^x$$

The italic roman “vee” v (from velocity of reaction) is the *rate of reaction* with units of $\text{mol L}^{-1} \text{ s}^{-1}$ whatever the order of reaction. The k is the *rate constant* whose units are determined by the order of reaction (x is the order with respect to H_2). Don’t confuse rate of reaction with rate constant. The following data for the rate of reaction is given in terms of seconds and pressure in the non-SI unit of torr, pressure is proportional to concentration at a constant temperature. A torr is a named unit for Evangelista Torricelli who invented the mercury in glass barometer (symbol Torr) is a convenient unit of pressure when using a mercury manometer with a ruler calibrated in millimetres as in the undergraduate chemistry lab, $750 \text{ Torr} = 1 \text{ bar}$ to three significant figures.

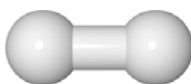


Figure 4.3: hydrogen molecule.

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

Firstly, plot a linear graph of the experimental data to determine x the order with respect to $[\text{H}_2]$. Secondly, find the rate constant for the reaction at the temperature of the H_2 gas and thirdly, calculate the rate of reaction for a pressure of 100 Torr.

[Jump to Solution 4 \(see page 89\)](#)

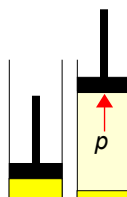
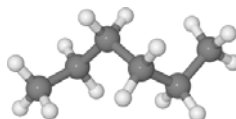
4.1.5 QUESTION 5: VAPOUR PRESSURE DATA FOR A LIQUID**Figure 4.4:** liquid vapour pressure.

Fig. 4.4 left, has a liquid added to a cylinder which is closed by a piston. The liquid and the apparatus are thermostated at a constant temperature. Fig. 4.4 right, some of the liquid has evaporated at equilibrium and pushes the piston out with a pressure p called the vapour pressure of the liquid at that temperature. The pressure of the vapour above a volatile liquid or volatile solid varies with temperature approximately as in the Clausius-Clapeyron equation, see section 1.2.7. The Clausius-Clapeyron equation may be integrated assuming that the enthalpy of vaporization is constant over a small temperature range (C is the constant of integration).

$$\ln p \approx -\frac{\Delta_{\text{vap}}H}{RT} + C \quad \text{Integrated Clausius-Clapeyron equation}$$

Where p is the vapour pressure, $\Delta_{\text{vap}}H$ is the enthalpy of vaporization of a liquid, a measure of the energy required to evaporate a mole of the liquid solvent to its vapour. The temperature T is in kelvin and C is the integration 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 degrees Celsius up to its boiling point at 68.7 °C. The units should be converted using 0 °C = 273.15 K. and 1 Torr = 133.32 Pa. Graphically determine the enthalpy of vaporization $\Delta_{\text{vap}}H$ in SI units.

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

**Figure 4.5:** hexane, hydrogen (light grey), and carbon (dark grey).

[Jump to Solution 5 \(see page 90\)](#)

4.2 WEEK 4 TUTORIAL SOLUTIONS

4.2.1 SOLUTION 1: PHOTOELECTRIC EXPERIMENTAL RESULTS

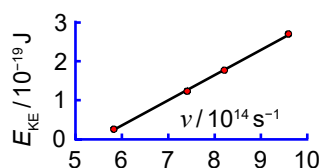



Figure 4.6: photoelectric experimental results.

Fig. 4.6, there is a linear dependence of the maximum kinetic energy of the ejected electron with the frequency of the light with a threshold frequency for the photoelectric effect. Although it is better to use a spreadsheet when possible, I am using this solution to explain the manual process (exam practice). To find the equation of the best-fit straight 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, or else you are wasting your time drawing a graph!



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$$\begin{aligned}
 (1) \quad (x_1, y_1) &= (6.00 \times 10^{14} \text{ s}^{-1}, 0.345 \times 10^{-19} \text{ J}) & (2) \quad (x_2, y_2) &= (9.00 \times 10^{14} \text{ s}^{-1}, 2.296 \times 10^{-19} \text{ J}) \\
 (3) \quad 0.345 \times 10^{-19} \text{ J} &= m(6.00 \times 10^{14} \text{ s}^{-1}) + c & (4) \quad 2.296 \times 10^{-19} \text{ J} &= m(9.00 \times 10^{14} \text{ s}^{-1}) + c \\
 (5) \quad 1.951 \times 10^{-19} \text{ J} &= m(3 \times 10^{14} \text{ s}^{-1}) & (6) \quad m &= 6.503 \times 10^{-34} \text{ J s} \\
 (7) \quad 2.641 \times 10^{-19} \text{ J} &= 9.7545 \times 10^{-19} \text{ J} + 2c & (8) \quad c &= -3.557 \times 10^{-19} \text{ J}
 \end{aligned}$$

The two points on the line are (1) and (2) which gives two simultaneous equations (3) and (4) respectively. The third decimal point is imprecise. Subtracting the two simultaneous equations (3) and (4). Subtracting these two simultaneous equations gives (5) then the gradient (6) of the best straight line. Adding the two simultaneous equations (7) and also substituting in the student's experimental value for the gradient leads to the intercept on the y -axis (8).

Planck's constant from the gradient (6) is $h = 6.503 \times 10^{-34} \text{ J s}$ whilst the accepted value for Planck's constant is $h = 6.626 \times 10^{-34} \text{ J s}$ the student measured value for Planck's constant has an accuracy of about 2%, so the gradient is reasonably accurate for an undergraduate teaching experiment with only four data points.

$$\begin{aligned}
 (9) \quad E_{\text{KE}} &= (6.503 \times 10^{-34} \text{ J s})\nu - (3.557 \times 10^{-19} \text{ J}) \\
 (10) \quad 0 &= (6.503 \times 10^{-34} \text{ J s})\nu_0 - (3.557 \times 10^{-19} \text{ J}) \\
 (11) \quad \nu_0 &= (3.557 \times 10^{-19} \text{ J}) / (6.503 \times 10^{-34} \text{ J s}) = 5.470 \times 10^{14} \text{ s}^{-1} \\
 (12) \quad \Phi &= (6.503 \times 10^{-34} \text{ J s})(5.470 \times 10^{14} \text{ s}^{-1}) = 3.557 \times 10^{-19} \text{ J}
 \end{aligned}$$

We have the equation of the line (9). The intercept on the x -axis (10) is ν_0 the value of x when $y = E_{\text{KE}} = 0$ and is calculated in (11). The work function Φ is $h\nu_0$ (12) and using the student's value for Planck's constant is $\Phi = 3.557 \times 10^{-19} \text{ J}$. The accepted value for the work function of sodium metal is $\Phi = 3.78 \times 10^{-19} \text{ J}$, so the student's work function has an accuracy of about 6% and needs some improvement to the apparatus and the experimental method with more data points over a wider frequency range.

[Return to Question 1 \(see page 80\)](#)

4.2.2 SOLUTION 2: PRESSURE-VOLUME EXPERIMENTAL DATA FOR CARBON DIOXIDE

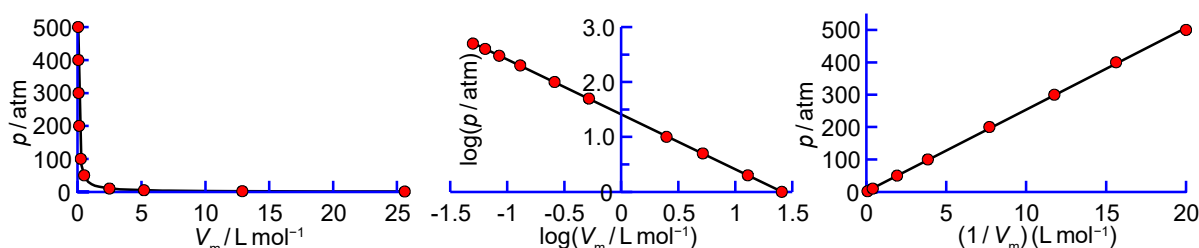


Figure 4.7: three pressure-volume plots for one mole of CO₂.

The plot of pressure against molar volume (Fig. 4.7, left) is a curve which the spreadsheet gives a best fit with a power function of $p = 25.66 \times V^{-1}$ this suggests a function of the form $p \propto 1/V$ similar to the ideal gas law. However, the p - V plot is not very useful at high pressures as the plot is nearly vertical and at low pressures it is nearly horizontal.

The data covers a wide range of values which suggest a log-log plot might be useful (Fig. 4.7, centre) this allows the data to be viewed more clearly and it also allows any “rogue” points in the experimental results to be noted for remeasuring and perhaps also for interpolating between data points. However, the log-log plot does *not* reflect any physical model for the p - V data.

As suggested by the power function $p = 25.66 \times V^{-1}$ that we noted earlier, we have plotted the pressure against the reciprocal of the volume (Fig. 4.7, right). This linear plot means that $p \times V$ equals a constant which agrees with the ideal gas law $pV = nRT$. Volumes are in litres and the pressures are in atmospheres and the gas constant in these units is equal to $R = 0.0820573 \text{ L atm K}^{-1} \text{ mol}^{-1}$ and at $T = 313 \text{ K}$ the gradient nRT should equal 25.7 L atm . The gradient of our plot is 25.2 L atm the difference is due to the slight scatter in the data. This experimental data fits the model of the ideal gas law over this range of p - V - T .

[Return to Question 2 \(see page 81\)](#)

4.2.3 SOLUTION 3: EXPERIMENTAL ARRHENIUS PLOT

Revise section 1.1.4 where we saw why the reciprocal $1/T$ is tabulated and plotted as $(1/T)(10^3 \text{ K})$. The rate constant has to be converted to a natural log. Logs are only for pure numbers not physical quantities. For example, $k/(10^{-3} \text{ s}^{-1}) = 5.26$ must be converted to $\ln(k/\text{s}^{-1}) = \ln(5.26 \times 10^{-3}) = -5.25$ note that any multiple *must* be incorporated *before* taking a log (or before taking an antilog) because the multiple is a part of the pure number.

T/K	293	298	303	308	313	318	323
$(1/T)(10^3 \text{ K})$	3.41	3.36	3.30	3.25	3.19	3.14	3.10
$k/(10^{-3} \text{ s}^{-1})$	5.26	7.56	14.4	22.7	48.3	62.1	119
$\ln(k/\text{s}^{-1})$	-5.25	-4.89	-4.24	-3.79	-3.03	-2.78	-2.13

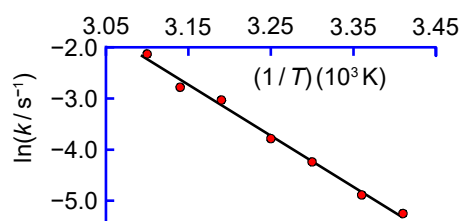


Figure 4.8: Arrhenius plot of $\ln(k)$ against $1/T$ data.

In Fig. 4.8 the Arrhenius plot is a straight line. The best-fit straight line is $y = -9.978x + 28.70$. 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 include the units and their multiples of the axes in the calculation, but as logs have to be pure numbers, so the units s^{-1} cannot be separated in the $\ln(k/s^{-1})$ term.

$$\begin{aligned} (1) \quad \frac{\ln(k/s^{-1})}{(1/T)(10^3 \text{ K})} &= -9.978 & (2) \quad \frac{\ln(k/s^{-1})}{1/T} &= -9.978 \times 10^3 \text{ K} \\ (3) \quad -\frac{E_a}{R} &= -9.978 \times 10^3 \text{ K} & (4) \quad E_a &= (9.978 \times 10^3 \text{ K})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \\ (5) \quad E_a &= 8.296 \times 10^4 \text{ J mol}^{-1} & (6) \quad E_a &= 82.96 \text{ kJ mol}^{-1} \end{aligned}$$

The intercept in Fig. 4.8 is $c = 28.70$ 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 multiples as the y -axis. Many first-order reactions have pre-exponential factors around 10^{12} - 10^{13} s^{-1} .

$$c = \ln(A/s^{-1}) = 28.70 \quad A/s^{-1} = \exp(28.70) = 2.912 \times 10^{12} \quad A = 2.912 \times 10^{12} \text{ s}^{-1}$$

To calculate the rate constant at $T = 283 \text{ K}$ then $(1/T) = (3.534 \times 10^{-3} \text{ K}^{-1})$ and so $x = (3.534 \times 10^{-3} \text{ K}^{-1})$, the equation for the best fit straight line is $y = -9.978x + 28.70$. Substitute $x = (3.534 \times 10^{-3} \text{ K}^{-1})$

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K^{-1}) into the equation for the best straight line in (7) which is evaluated in (8). Take antilogs of both sides in (9). We may now move the units across to the right hand side (10).

$$\begin{aligned}
 (7) \quad \ln(k/\text{s}^{-1}) &= (-9.978 \times 10^3 \text{ K})(3.534 \times 10^{-3} \text{ K}^{-1}) + 28.70 & (8) \quad \ln(k/\text{s}^{-1}) &= -6.562 \\
 (9) \quad k/\text{s}^{-1} &= \exp(-6.562) = 1.413 \times 10^{-3} & (10) \quad k &= 1.413 \times 10^{-3} \text{ s}^{-1}
 \end{aligned}$$

[Return to Question 3 \(see page 82\)](#)

4.2.4 SOLUTION 4: EXPERIMENTAL DETERMINATION OF THE ORDER OF A CHEMICAL REACTION

$$(1) \quad v = k[\text{H}_2]^x \quad (2) \quad \log(v) = \log(k[\text{H}_2]^x) \quad (3) \quad \log(v) = \log(k) + \log[\text{H}_2]^x$$

$$\overbrace{\log(v)}^y = \overbrace{\log(k)}^c + \overbrace{\frac{1}{x}}^m \overbrace{\log[\text{H}_2]}^x$$

From the rate law (1) $v = k[\text{H}_2]^x$ take logs (2) on both sides of the equation. (3) Expand out the log of the product of two terms as the sum of two log terms. Bring down the exponent x of the log gives us a linear equation $y = c + mx$ shown above. Don't confuse the order of reaction x and the general variable as in x -axis.

$v/(10^{-2} \text{ Torr s}^{-1})$	4.20	3.40	2.60	2.05	1.65
$v/\text{Torr s}^{-1}$	4.20×10^{-2}	3.40×10^{-2}	2.60×10^{-2}	2.05×10^{-2}	1.65×10^{-2}
$\log(v/\text{Torr s}^{-1})$	-1.377	-1.469	-1.585	-1.688	-1.783
p/Torr	400	316	248	196	155
$\log(p/\text{Torr})$	2.60	2.50	2.39	2.29	2.19

In the log of the rate of reaction we *must* take any multiplier over to the right hand side before taking logs as the multiplier is part of the pure number.

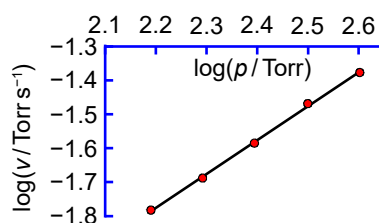


Figure 4.9: $\log(\text{rate of reaction})$ versus $\log(\text{pressure})$.

The equation of the best straight line is $y = 1.0005x - 3.9772$. The order of reaction is the gradient = 1.0005 which is clearly first-order in H_2 within the scatter of the limited data. The rate constant at the temperature of the measurements is equal to the intercept $c =$

-3.9772 . The y -axis is a log of a pure number so for the first-order rate constants $c = \log(k/s^{-1}) = -3.9772$. Taking antilogs of both sides $k/s^{-1} = 10^{-3.9772} = 1.0534 \times 10^{-4}$ and moving the units across $k = 1.0534 \times 10^{-4} s^{-1}$.

- (1) $\log(v/\text{Torr s}^{-1}) = 1.0005 \times \log(p/\text{Torr}) - 3.0772$
- (2) $\log(v/\text{Torr s}^{-1}) = 1.0005 \times 2 - 3.0772 = -1.9762$
- (3) $v/\text{Torr s}^{-1} = 10^{-1.9762} = 1.0563 \times 10^{-2}$
- (4) $v = 1.0563 \times 10^{-2} \text{ Torr s}^{-1}$

To calculate the rate of reaction for a $p = 100$ Torr we start with the equation of the best straight line (1). In (2) substitute $\log(p/\text{Torr}) = \log(100) = 2$ and calculate the $\log(\text{rate})$. Take antilogs in (3) and then (4) move the units to the right hand side.

[Return to Question 4 \(see page 83\)](#)

4.2.5 SOLUTION 5: VAPOUR PRESSURE DATA FOR A LIQUID

temp/ $^{\circ}\text{C}$	-53.9	-25	-2.3	15.8	49.6	68.7
T/K	219.25	248.15	270.85	288.95	322.75	341.85
$(1/T)(10^3 \text{ K})$	4.561	4.030	3.692	3.461	3.098	2.925
p/Torr	1	10	40	100	400	760
p/Pa	133.32	1333.2	5332.8	13332	53328	101325
$\ln(p/\text{Pa})$	4.8928	7.1953	8.5816	9.4979	10.8842	11.5261

In order to have a linear graph we convert the temperatures from degrees Celsius to kelvin and take the reciprocal $(1/T)(10^3 \text{ K})$ and the pressures in Torr to pascals then take the natural-log $\ln(p/\text{Pa})$. Fig. 4.10 has a best-fit straight line of $y = -4.0464x + 23.4428$ but the axes cross a long way from the origin.

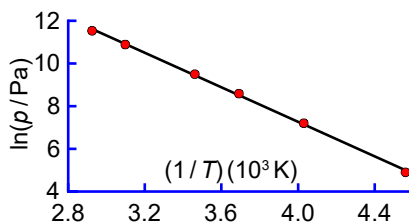


Figure 4.10: hexane vapour pressure.

- (1) $\frac{\ln(p/\text{Pa})}{1/T(10^3 \text{ K})} = -4.0464$
- (2) $\frac{\ln(p/\text{Pa})}{1/T} = -4.0464 \times 10^3 \text{ K}$
- (3) $-\frac{\Delta_{\text{vap}} H}{R} = -4.0464 \times 10^3 \text{ K}$
- (4) $\Delta_{\text{vap}} H = (4.0464 \times 10^3 \text{ K})(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})$
- (5) $\Delta_{\text{vap}} H = 3.3644 \times 10^4 \text{ J mol}^{-1}$
- (6) $\Delta_{\text{vap}} H = 33.64 \text{ kJ mol}^{-1}$

The enthalpy of vaporization is calculated from the gradient (1) of the best straight line. The multiplier and units for the reciprocal temperature are moved across in (2) but the log term cannot be separated as logs have to be a pure number. The Clausius-Clapeyron equation has a gradient (3) of $m = -\Delta_{\text{vap}} H/R$ and in (4) negative signs cancel and the gas constant is moved over to the right. The student's measured value for the enthalpy of vaporization of hexane (6) is higher by about 8% than the accepted literature value of 31.1 kJ mol^{-1} (Acree & Chickos, 2017) and possible improvements to the experimental method such as many more data points and also possible improvements to the apparatus should be considered.

[Return to Question 5 \(see page 84\)](#)

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5 WEEK 5: CHEMISTRY AND DIFFERENTIATION 1

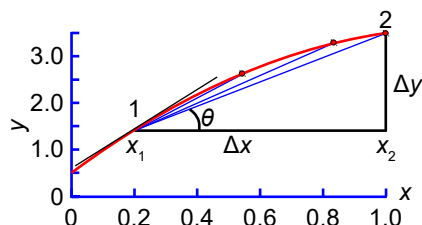


Figure 5.1: differential of a function at the point x_1 .

A function $y = f(x)$ has $\tan(\theta) = \Delta y / \Delta x$ between the points 1 and 2. As point 2 approaches point 1 the $\tan(\theta)$ increases as Δy and Δx change as shown by the blue lines. We reach in the limit the differential (or derivative) dy/dx at point x_1 which may also be written as $f'(x_1)$ and $\tan(\theta)$ approaches the slope of the tangent to the function at x_1 the black line.

$$f'(x_1) = \lim_{\Delta x \rightarrow 0} \frac{\Delta y}{\Delta x} = \frac{dy}{dx}$$

Definition: differentiation of a function at x_1

The function used in Fig. 5.1 is $y = 0.5 + 5x - 2x^2$ so $dy/dx = 5 - 4x$ and the derivative at $x_1 = 0.2$ is equal to $dy/dx = 5 - 4 \times 0.2$ and the derivative of our function at $x_1 = 0.2$ is $f'(0.2) = 4.2$.

5.1 WEEK 5 TUTORIAL QUESTIONS

5.1.1 QUESTION 1: MOLECULES OF A GAS

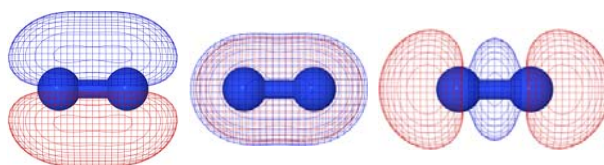


Figure 5.2: N₂ π -bond in-plane, π -bond out-of-plane, and σ -bond.

Fig. 5.2 shows from the left the two π -bonds at right angles to one another and the σ -bond which constitute the N₂ triple bond. Let us start by considering a simple maths situation that perhaps familiar from school or college. Consider a N₂ molecule at 298 K moving with a typical velocity $v = 515 \text{ m s}^{-1}$. The velocity at any point in time is the derivative of the distance-time curve (d - t graph). Note the difference between the differential operators

d in roman upright text and the variable symbol in italic d for distance, operators operate on variables such as d or t .

$$v = \frac{dd}{dt} \quad \text{Velocity is the differential of distance with time}$$

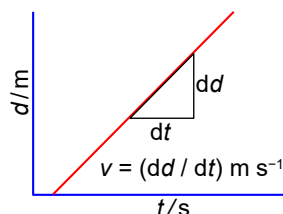


Figure 5.3: plot of uniform motion in a straight line.

Calculate the time for the nitrogen molecule to travel a distance of 10 km in a straight line with no collisions (corresponds to an extremely low pressure as in the earth's outer atmosphere).

[Jump to Solution 1 \(see page 97\)](#)

5.1.2 QUESTION 2: MOLECULES OF A GAS

What if the N_2 molecule (or any other object) is changing its velocity with time? Acceleration (a) is the differential of the velocity-time curve (v - t graph) at a particular point in time. But as velocity is the differential of distance with time then acceleration is also the *second* derivative of the distance-time curve at a particular point in time. For uniform motion in a straight line the acceleration is zero.

$$a = \frac{dv}{dt} = \frac{d}{dt} \left(\frac{dd}{dt} \right) = \frac{d^2d}{dt^2} \quad \text{Acceleration is the differential of the velocity with time}$$

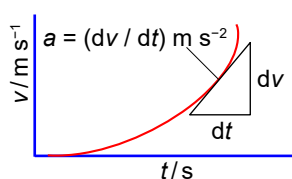


Figure 5.4: non-uniform motion in a straight line.

The N_2 molecule collides with another molecule in a collision lasting 100 ps (picoseconds where $1 \text{ ps} = 10^{-12} \text{ s}$). 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 \(see page 97\)](#)

5.1.3 QUESTION 3: MOLECULES OF A GAS

The unified atomic mass unit (symbol u) also called a dalton (symbol Da) is $u = 1.6605 \times 10^{-27}$ kg to five significant figures, note it is in kilograms not grams and is in roman type not italic. The most common isotopic form of nitrogen is $^{14}\text{N}_2$ which has a mass of 2×14.0031 u = 28.0062 u. The units of force comes from mass times acceleration and are kg m s^{-2} it is a named unit called the newton with a lower case “n” (symbol N) whereas Sir Isaac’s surname is Newton. Calculate the force in newtons which was required to bring about the acceleration of section 5.1.2.

$$F = m \times a$$

Definition: force equals mass times acceleration

[Jump to Solution 3 \(see page 97\)](#)

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



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travels at 630 m s^{-1} in the *opposite* direction, assume the wall of the container has “infinite” mass compared with the N_2 molecule. What has been the N_2 molecule’s acceleration in this collision?

[Jump to Solution 4 \(see page 98\)](#)

5.1.5 QUESTION 5: MAXWELL-BOLTZMANN DISTRIBUTION OF SPEEDS OF GAS MOLECULES

At normal pressures of about 1 bar and ambient temperatures of around 298 K the time between a gas phase molecule colliding is approximately 10^{-10} - 10^{-9} s or 0.1-1 ns (10^{-9} s is a nanosecond, symbol ns). Each of these collisions alters the speed and direction of the molecules. For a gas consisting of identical molecules the fraction $f(c)$ of them with a *speed* c (ignoring the direction) is given by the Maxwell-Boltzmann distribution of speeds.

$$f(c) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} c^2 \exp\left(-\frac{mc^2}{2k_B T}\right) \quad \text{Maxwell-Boltzmann speed distribution}$$

Where m is the molecular mass (the mass of one molecule in kg), k_B is Boltzmann’s constant (the gas constant per molecule) $k_B = R/N_A = 1.38065 \times 10^{-23} \text{ J K}^{-1}$. The subscript “B” is to remove any confusion with the symbol for rate constant or force constant. T the temperature of the gas in kelvin.

The Maxwell-Boltzmann speed distribution of a gas is rather a frightening equation when first seen but we are now going to use a common trick which helps make the equation look less daunting. For a given type of molecule at a constant temperature the first two terms $4\pi(m/2\pi k_B T)^{3/2}$ are constant so we can call them A , also in the exponential $m/2k_B T$ is constant so let us write the exponential as $\exp(-Bc^2)$ where $B = m/2k_B T$ is constant.

$$f(c) = Ac^2 \exp(-Bc^2)$$

For simplicity and in order to curve sketch let’s arbitrarily assume the constants $A = B = 1$. Firstly, sketch the curves of c^2 then $\exp(-c^2)$ and finally the product $c^2 \times \exp(-c^2)$ against c using a spreadsheet (curve sketching a graph means show the basic shape of it). Secondly, differentiate the equation with respect to c and find the maximum of the graph which is called the most probable speed c_{mp} of the molecules.

[Jump to Solution 5 \(see page 98\)](#)

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.

$t/10^{-3} \text{ s}$	0.00	2.00	4.00	6.00	8.00	10.0
$[A]/\text{mol L}^{-1}$	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.

$$v = -\frac{d[A]}{dt}$$

Definition: rate of reaction for a single reactant species A.

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, either by hand or using a spreadsheet. Secondly, draw tangents to the graph and find values for the rate of reaction at $t = 0$, 2.5×10^{-3} , 5.0×10^{-3} , and 7.5×10^{-3} s. What conclusion can you draw from these rates of reaction as a function of time?

[Jump to Solution 6 \(see page 101\)](#)



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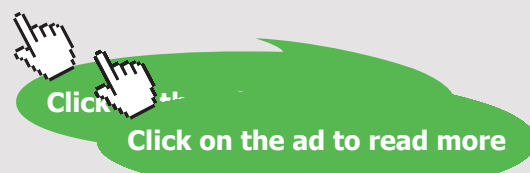
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5.2 WEEK 5 TUTORIAL SOLUTIONS

5.2.1 SOLUTION 1: MOLECULES OF A GAS

$$(1) \ v = \frac{d}{t} \quad (2) \ t = \frac{d}{v} \quad (3) \ t = \frac{10^4 \text{ m}}{515 \text{ m s}^{-1}} \quad (4) \ t = 19.4 \text{ s}$$

For uniform motion in a straight line the differential dd/dt is constant with time, that is the velocity is constant so $v = d/t$ as shown in (1) above which is rearranged in (2) to make time the subject. Substitute the physical quantities for the variables (3), it is advisable to carry out calculations in the base units (m not km) so that the units may cancel out correctly. (4) Notice how in the *absence* of any collision a molecule can travel a long distance very quickly, 10 km in 19 s. The absence of collisions corresponds to very low pressures as in the earth's atmosphere above about 700 km (exosphere) where most satellites are in orbit. Of course at 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 \(see page 92\)](#)

5.2.2 SOLUTION 2: MOLECULES OF A GAS

The acceleration in this 100 ps collision of molecules is calculated below. Note when calculating a change in a variable by convention it is defined as *final* minus *initial* value of the variable. Molecules are capable of very rapid acceleration and deceleration by means of collisions.

$$a = \frac{dv}{dt} \quad a = \frac{630 \text{ m s}^{-1} - 515 \text{ m s}^{-1}}{100 \times 10^{-12} \text{ s}} \quad a = 1.15 \times 10^{12} \text{ m s}^{-2}$$

[Return to Question 2 \(see page 93\)](#)

5.2.3 SOLUTION 3: MOLECULES OF A GAS

$$(1) \ F = m \times a \quad (2) \ F = (28.0062 \text{ u})(1.6605 \times 10^{-27} \text{ kg/u})(1.15 \times 10^{12} \text{ m s}^{-2}) \\ (3) \ F = 5.35 \times 10^{-14} \text{ kg m s}^{-2} \quad (4) \ F = 5.35 \times 10^{-14} \text{ N}$$

As expected it only takes a minute force to accelerate the N_2 molecule because of its small mass. How large is a newton of force? An average-sized apple (about 100 g) in the earth's

gravitational field exerts about one newton of force, which we measure as the apple's weight. A person of 80.7 kg weight exerts a gravitational force of 791 N.

[Return to Question 3 \(see page 94\)](#)

5.2.4 SOLUTION 4: MOLECULES OF A GAS

$$a = \frac{dv}{dt} \quad a = \frac{(630 \text{ m s}^{-1}) - (-630 \text{ m s}^{-1})}{100 \times 10^{-12} \text{ s}} \quad a = \frac{1260 \text{ m s}^{-1}}{1.00 \times 10^{-10} \text{ s}} \quad a = 1.26 \times 10^{13} \text{ m s}^{-2}$$

The final velocity is in the opposite direction to the initial velocity, note the difference between the operation of subtraction and a negative quantity. Collisions with the vessel walls as well as molecule-molecule collisions cause molecules to undergo very rapid acceleration or deceleration.

[Return to Question 4 \(see page 94\)](#)

5.2.5 SOLUTION 5: MAXWELL-BOLTZMANN DISTRIBUTION OF SPEEDS OF GAS MOLECULES

	A	B	C	D
1	c	c^2	$\exp(-c^2)$	$c^2 \exp(-c^2)$
2	0	0	1	0
3	0.01	0.0001	0.999900004999833	9.99900004999833E-05
4	0.02	0.0004	0.999600079989334	0.000399840031996
5	0.03	0.0009	0.999100404878527	0.000899190364391
6	0.04	0.0016	0.998401279317606	0.001597442046908

Table 5.1: the first few terms of the spreadsheet of the Maxwell-Boltzmann equation.

Cells A2 to A6 were manually typed into the spreadsheet. A2 to A6 were then selected with the mouse and the bottom-right handle of the selection was dragged down the A column to dynamically expand the selection down to $c = 3.2$. Then the cells B2 = A2^2, C2 = EXP(-B2), and D2 = B2×C2 where manually typed. Then B2, C2, and D2 were selected with the mouse and the bottom-right handle of the selection was dragged down the D column to dynamically expand the selection down to the row with $c = 3.2$.

Fig. 5.5 shows the shapes of the two constituent curves in blue and green and the product of these two terms is the shape of the Maxwell-Boltzmann speed distribution of molecules

in red. Remember for simplicity and in order to curve sketch we have arbitrarily assumed the constants $A = B = 1$. The Maxwell-Boltzmann speed distribution is the product of two terms in c that is $f(c) = Ac^2\exp(-Bc^2)$. The c^2 term (green) *increase* from zero upwards with increasing c . The negative exponential term (blue) $\exp(-Bc^2)$ *decrease* from 1.0 downwards asymptotically towards zero with increasing c . So the $f(c) = Ac^2\exp(-Bc^2)$ being the product of these two terms in red will start from zero at $c = 0$, then drop back to zero at large values of c , and at intermediate values of c the fraction will pass through a maximum.

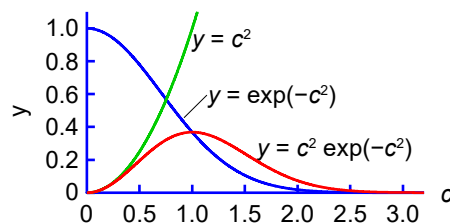


Figure 5.5: curve sketches of c^2 , $\exp(-c^2)$, and $c^2\exp(-c^2)$ against c .

To find the most probable speed, the Maxwell-Boltzmann equation must be differentiated, and $df(c)/dc$ and then set equal to zero. As the Maxwell-Boltzmann equation is the product of two terms involving c we must use the “product rule for differentiation”.

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English for 16
years but...
...I finally
learned to
speak it in just
six lessons”

Jane, Chinese architect

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$$\frac{d(uv)}{dx} = u \frac{dv}{dx} + v \frac{du}{dx} \quad \text{The product rule for differentiation}$$

Let's substitute $u = Ac^2$ and $v = \exp(-Bc^2)$ so that $f(c) = uv$ and use the *product rule* for the differentiation of a product of two functions.

$$u = Ac^2 \quad \frac{du}{dc} = 2Ac \quad v = \exp(-Bc^2) \quad \frac{dv}{dc} = (-2Bc) \exp(-Bc^2)$$

The dv/dc term has come from using the general form for the differential of an exponential term using the *chain rule* of differentiation.

$$\frac{dy}{dx} = \frac{dy}{dn} \times \frac{dn}{dx} \quad \text{Chain rule for differential of a function } y = f(n) \text{ where } n = f(x)$$

$$\frac{de^n}{dx} = \frac{dn}{dx} e^n \quad \text{The chain rule applied to } y = e^n \text{ where } n = f(x)$$

(1) Differentiate the Maxwell-Boltzmann speed distribution using the product rule for differentiation and the chain rule for derivative of an exponential. (2) We take the common factor $\exp(-Bc^2)$ outside the bracket and at the maximum the derivative must be equal to zero.

$$(1) \quad \frac{df(c)}{dc} = (Ac^2)(-2Bc)\exp(-Bc^2) + \exp(-Bc^2)(2Ac)$$

$$(2) \quad \frac{df(c)}{dc} = [(Ac^2)(-2Bc) + (2Ac)] \exp(-Bc^2) = 0$$

$$(3) \quad (Ac_{mp}^2)(-2Bc_{mp}) + (2Ac_{mp}) = 0$$

$$(4) \quad 2ABc_{mp}^3 = 2Ac_{mp} \quad (5) \quad c_{mp} = \sqrt{\frac{1}{B}}$$

In (2) for $df(c)/dc$ to be equal to zero either $\exp(-Bc^2) = 0$, which is unrealistic as this only happens at the asymptote of infinite speed, or alternatively the term in brackets equals zero. (3) The term in brackets is equal to zero at the maximum corresponding to the most probable speed. Cleaning up (4) gives us (5) the expression for the most probable speed as the square root of the reciprocal of B . Substituting for B gives the maximum of the speed distribution, the most probable speed c_{mp} . Notice the most probable speed of ideal gas molecules depends only on their mass and the temperature but not on the nature of the molecule.

$$c_{mp} = \sqrt{\frac{2k_B T}{m}} \quad \text{Definition: most probable speed of gas molecule}$$

[Return to Question 5 \(see page 95\)](#)

5.2.6 SOLUTION 6: MEASURING RATES OF REACTION FROM CONCENTRATION DATA

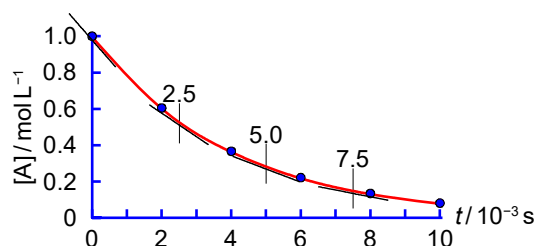


Figure 5.6: reactant concentration versus time.

Fig. 5.6 shows the reagent concentration against time graph and the gradients to the curve.

$t/10^{-3} \text{ s}$	0	2.5	5.0	7.5
$\frac{d[A]/\text{mol L}^{-1}}{dt/10^{-3} \text{ s}^{-1}}$	-0.25133	-0.13410	-0.071530	-0.038160
$v/\text{mol L}^{-1} \text{ s}^{-1}$	251.33	134.10	71.530	38.160

The spreadsheet gradients from Graph 4.4.2 (Johansen 2013) which are negative, however, rates of chemical reactions are defined as always positive. The gradient has units and a multiplier for the time, for example, at zero time the spreadsheet gradient is $d[A]/\text{mol L}^{-1}/dt/(10^{-3} \text{ s}^{-1}) = -0.25133$, the rate of disappearance of A is $-d[A]/dt = 0.25133 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$. The rate of reaction at zero time is $v = 251.33 \text{ mol L}^{-1} \text{ s}^{-1}$ which is tabulated above as a pure number as $v/\text{mol L}^{-1} \text{ s}^{-1} = 251.33$.

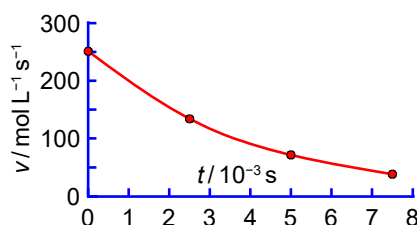


Figure 5.7: rate of reaction versus time.

Fig. 5.7 plots the rate of reaction against time. The rate of reaction v decreases with time because the concentration of reactant [A] is decreasing as it is consumed in forming the product.

[Return to Question 6 \(see page 96\)](#)

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 (called the intermolecular interaction) is given by the Lennard-Jones equation.

$$V = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \text{ Lennard-Jones potential}$$

Where V is the potential energy of the interacting molecules, r is the distance between the two molecules' centres of mass, ϵ (italic Greek epsilon) is the depth of the potential well and σ is the value of r for $V = 0$. The 6th-power term describes the long-range *attraction* between the molecules due to the van der Waals or dispersion force plus any dipole-dipole force and any dipole-induced dipole force, it lowers the potential energy (the term is negative). The 12th-power term represents the short-range *repulsion* between the molecules (the term is positive) from the overlap of their electron orbitals when the distance between the molecules becomes small, it rapidly increases the potential energy. Fig. 6.1 shows the MOPAC2016 (PM7) calculated structure for the minimum of the potential energy well for the interaction between two N_2 molecules.

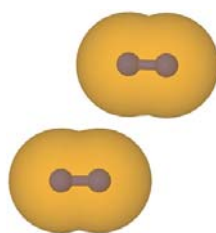


Figure 6.1: calculated minimum energy structure of two nitrogen molecules.

In Fig. 6.1 the surfaces are the van der Waals “size” of the molecules, in this relative position there is a balance of the repulsive and the attractive forces between the molecules. Use a spreadsheet to plot the following three graphs: firstly, the attractive long range potential $V_{\text{at}} = -4\epsilon(\sigma/r)^6$, secondly, the short range repulsive potential $V_{\text{re}} = 4\epsilon(\sigma/r)^{12}$, and thirdly, the combined Lennard-Jones potential V_{LJ} for the interaction between two N_2 molecules.

The N_2 parameters are $\varepsilon = 763.6 \text{ J mol}^{-1}$ and $\sigma = 3.919 \times 10^{-10} \text{ m}$ (3.919 \AA) and plot for intermolecular distances from 3.8 \AA to 10 \AA in steps of 0.01 \AA .

[Jump to Solution 1 \(see page 106\)](#)

6.1.2 QUESTION 2: INTERMOLECULAR INTERACTIONS

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

For a given molecular interaction the variables in the Lennard-Jones equation are V and r . Calculate the derivatives dV/dr then differentiate the first derivative with respect to r to find the second derivative d^2V/dr^2 for the intermolecular potential between N_2 molecules.

[Jump to Solution 2 \(see page 108\)](#)

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 \(see page 108\)](#)

6.1.4 QUESTION 4: CHANGES IN pH

$$\text{pH} = -\log[\text{H}^+] \quad \text{Definition: pH of a solution}$$

Firstly, show that $d(\text{pH})/d[\text{H}^+]$, the small change in pH arising from a small change in $[\text{H}^+]$ is proportional to the ratio $d[\text{H}^+]/[\text{H}^+]$. Secondly, a solution originally with $[\text{H}^+] = 0.02 \text{ mol L}^{-1}$ had an additional concentration of $d[\text{H}^+] = 5 \times 10^{-4} \text{ mol L}^{-1}$ added to it, calculate the change in pH, $d(\text{pH})$.

[Jump to Solution 4 \(see page 109\)](#)

6.1.5 QUESTION 5: DIFFERENTIATION OF THE ARRHENIUS EQUATION

$$k = A \exp(-E_a/RT)$$

The rate constant k for a chemical reaction is related to the temperature T by the Arrhenius equation. Where the pre-exponential factor A and activation energy E_a are constants for a given chemical reaction, R is the gas constant. A particular biochemical reaction is second-order, first let's find the units for the second-order rate constant. The units for *any* rate of reaction v are concentration per time, $\text{mol L}^{-1} \text{s}^{-1}$ and all concentrations are mol L^{-1} . The dimensional analysis below gives the units of k as $\text{L mol}^{-1} \text{s}^{-1}$ for a second-order reaction.

$$(1) \quad \overbrace{v}^{\text{mol L}^{-1} \text{s}^{-1}} = k \overbrace{[A][B]}^{\text{mol}^2 \text{L}^{-2}} \quad (2) \quad \overbrace{k}^{\text{L mol}^{-1} \text{s}^{-1}} = \overbrace{v}^{\text{mol L}^{-1} \text{s}^{-1}} / \overbrace{[A][B]}^{\text{mol}^2 \text{L}^{-2}}$$

If $k = 20 \text{ L mol}^{-1} \text{s}^{-1}$ at $T = 300 \text{ K}$ and $E_a = 50 \text{ kJ mol}^{-1}$ for a particular biochemical reaction calculate the pre-exponential factor A . Differentiate the Arrhenius equation with respect to T and then find the change in the value of k when T increases by 1 K to 301 K. Remember to use the base unit of $E_a = 50000 \text{ J mol}^{-1}$ in the calculation and not its multiple of 50 kJ mol^{-1} .

[Jump to Solution 5 \(see page 109\)](#)



What do you want to do?

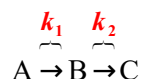
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6.1.6 QUESTION 6: CONSECUTIVE CHEMICAL REACTIONS

Consecutive reactions are where two or more chemical reactions follow on from one another. Consecutive reactions are very common in all branches of chemistry and biochemistry. The simplest type is where both reactions are kinetically first-order.



The molecule A is the reactant, C the product, and B is called an *intermediate*. If k_1 and k_2 are first-order rate constants and assuming that we start at time zero with pure A and no B or C present then this mechanism gives the concentration of the intermediate at a later time t as follows. Where $[A]_0$ is the initial concentration of A. Find the time t_{\max} at which $[B]$ is a maximum $[B]_{\max}$.

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$$

[Jump to Solution 6 \(see page 110\)](#)

6.1.7 QUESTION 7: CONSECUTIVE CHEMICAL REACTIONS

For a first-order reaction the reactant concentration varies with time as $[A] = [A]_0 \exp(-k_1 t)$ at a constant temperature.

- 1) Construct a spreadsheet of the following data, $[B]$, t , and $d[B]/dt$ (from section 6.2.6). The time should run from zero to one second in intervals of 0.1 s.
- 2) Assuming that $[A]_0 = 1 \text{ mol L}^{-1}$, $k_1 = 7.0 \text{ s}^{-1}$ and $k_2 = 5.0 \text{ s}^{-1}$ draw a graph of $[A]$, $[B]$, and $[C]$ versus time.
- 3) Draw a graph of $d[B]/dt$ versus t and find t_{\max} on your graph.
- 4) Find the value of $[B]_{\max}$ From your graph.

[Jump to Solution 7 \(see page 111\)](#)

6.1.8 QUESTION 8: CONSECUTIVE CHEMICAL REACTIONS: THE STEADY STATE APPROXIMATION

For two consecutive first-order chemical reactions $A \rightarrow B \rightarrow C$ consider each of the three terms in the equation below for the intermediate concentration $[B]$ and show that if k_1 is

much smaller than k_2 ($k_1 \ll k_2$) then $[B]$ will be a small concentration and also $d[B]/dt$ will be relatively constant in *absolute* terms compared with the reactant and product concentrations.

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$$

[Jump to Solution 8 \(see page 113\)](#)

6.1.9 QUESTION 9: CONSECUTIVE CHEMICAL REACTIONS WITH A RATE DETERMINING STEP

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$$

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 ($k_1 \gg k_2$), that is, the reverse of the situation in section 6.1.8.

[Jump to Solution 9 \(see page 115\)](#)

6.2 WEEK 6 TUTORIAL SOLUTIONS

6.2.1 SOLUTION 1: INTERMOLECULAR INTERACTIONS

$$V = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

	A	B	C	D
1	$r / \text{\AA}$	$V_{LJ} / \text{J mol}^{-1}$	$V_{at} / \text{J mol}^{-1}$	$V_{re} / \text{J mol}^{-1}$
2	3.80	746.92	-3675.16	4422.07
3	3.81	667.13	-3617.66	4284.79
4	3.82	590.90	-3561.21	4152.11
5	3.83	518.09	-3505.78	4023.87

Table 6.1: the first few terms of the Lennard-Jones spreadsheet.

The spreadsheet (Table 6.1) has the intermolecular distance varying from 3.8 Å to 10 Å in steps of 0.01 Å. The distances A1 to A5 are manually typed into the spreadsheet. Cells A1 to A5 are selected with the mouse and the right-bottom handle is dragged down the A column until 10 Å is reached and the mouse button is released. The formulae B2 to D2 are typed manually as $B2 = 4*763.6*(3.919/A2)^{12} - (3.919/A2)^6$, $C2 = -4*763.6*(3.919/$

$A2)^6$, and $D2 = 4 \times 763.6 \times (3.919/B3)^{12}$. Cells B2 to D2 are selected with the mouse and the right-bottom handle is dragged down the D column until the row with $r = 10 \text{ \AA}$ is reached and the mouse button is released.

Fig. 6.2 shows the repulsive part of the potential in black, the attractive part of the potential in blue, the combined Lennard-Jones potential is the sum of these two terms is shown in red. Note that both $\sigma = 3.919$ and the intermolecular distance r are in angstroms hence the units cancel, the potential energy is in J mol^{-1} . The two parameters give the position where the potential energy is zero $\sigma = 3.919 \text{ \AA}$, and from the spreadsheet the potential energy well depth is $\epsilon = 763.6 \text{ J mol}^{-1}$ at an intermolecular distance of $r_{\min} = 4.40 \text{ \AA}$ to a precision of 0.01 \AA .

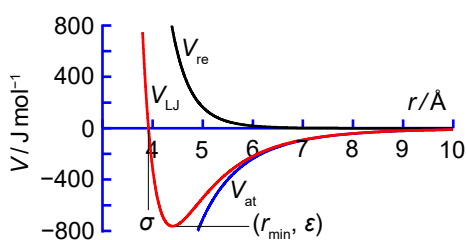


Figure 6.2: Lennard-Jones potential for N_2 .

[Return to Question 1 \(see page 102\)](#)

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6.2.2 SOLUTION 2: INTERMOLECULAR INTERACTIONS

$$\begin{aligned}
 (1) \quad V &= 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & (2) \quad V &= 4\epsilon (\sigma^{12} r^{-12} - \sigma^6 r^{-6}) \\
 (3) \quad \frac{dV}{dr} &= 4\epsilon (-12\sigma^{12} r^{-13} + 6\sigma^6 r^{-7}) & (4) \quad \frac{dV}{dr} &= 4\epsilon \left(-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right) \\
 (5) \quad \frac{d^2V}{dr^2} &= 4\epsilon (156\sigma^{12} r^{-14} - 42\sigma^6 r^{-8}) & (6) \quad \frac{d^2V}{dr^2} &= 4\epsilon \left(\frac{156\sigma^{12}}{r^{14}} - \frac{42\sigma^6}{r^8} \right)
 \end{aligned}$$

Starting with the Lennard-Jones potential (1) write the denominators as numerators (2), the first derivative gives (3) is converted in (4) to the r^{-13} and r^{-7} terms as denominators. A similar approach is used to calculate the second derivative. From the first derivative of the Lennard-Jones potential (3), the second derivative is (5) and is rewritten with the r^{-14} and r^{-8} as denominators in (6).

[Return to Question 2 \(see page 103\)](#)

6.2.3 SOLUTION 3: INTERMOLECULAR INTERACTIONS

$$\begin{aligned}
 (1) \quad \frac{dV}{dr} &= 4\epsilon \left(-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right) = 0 & (2) \quad \frac{12\sigma^{12}}{r_{\min}^{13}} &= \frac{6\sigma^6}{r_{\min}^7} & (3) \quad \frac{r_{\min}^{13}}{r_{\min}^7} &= \frac{12\sigma^{12}}{6\sigma^6} \\
 (4) \quad r_{\min}^6 &= 2\sigma^6 & (5) \quad r_{\min}^6 &= 2 \times 3.919^6 & (6) \quad r_{\min} &= 4.3989 \text{ \AA}
 \end{aligned}$$

To find the intermolecular separation at which the potential V is at a minimum we use the first derivative (1) set equal to zero and for clarity I have not shown the units in the evaluations. In equation (1) either 4ϵ equals zero (which it cannot be as the well depth epsilon ϵ is a non-zero parameter) or the term in brackets equals zero. Steps (2) to (6) uses algebra to calculate the minimum intermolecular distance from the term in brackets in (1). If σ is in angstroms then r_{\min} is also in angstroms and $r_{\min} = 4.40 \text{ \AA}$ (to two decimal places) agrees with our spreadsheet graph and is the separation of *two* N_2 molecules centre of masses at the minimum potential energy of $-763.6 \text{ J mol}^{-1}$ which is a lower energy than the two isolated N_2 molecules which have an intermolecular potential energy of 0 J mol^{-1} . The average thermal energy is $(3/2)RT = 3718 \text{ J mol}^{-1}$ at 298.15 K so such “dimers” will be very quickly broken at normal pressure but will persist for longer times at low pressures (less collisions) or lower temperatures (less energetic collisions).

[Return to Question 3 \(see page 103\)](#)

6.2.4 SOLUTION 4: CHANGES IN pH

$$\begin{aligned} (1) \text{ pH} &= -\frac{\ln[\text{H}^+]}{2.3026} & (2) \frac{d(\text{pH})}{d[\text{H}^+]} &= -\frac{1}{2.3026[\text{H}^+]} \\ (3) d(\text{pH}) &= -\frac{d[\text{H}^+]}{2.3026[\text{H}^+]} & (4) d(\text{pH}) &= -\frac{5 \times 10^{-4} \text{ mol L}^{-1}}{2.3026 \times 0.02 \text{ mol L}^{-1}} = -0.011 \end{aligned}$$

In order to differentiate the \log_{10} equation, $\text{pH} = -\log[\text{H}^+]$ we must first convert it to natural logs, (see section 3.1.4) using the conversion $2.3026 = \ln(x)/\log(x)$ which gives (1). In (2) we can now differentiate the pH with respect to hydrogen ion concentration. We separate the variables of the derivative in (3) and take $d[\text{H}^+]$ over to the right. Substitute of the values for the variables in (4). As expected *increasing* the hydrogen ion concentration leads to a *decrease* in pH.

[Return to Question 4 \(see page 103\)](#)

6.2.5 SOLUTION 5: DIFFERENTIATION OF THE ARRHENIUS EQUATION

$$\begin{aligned} (1) k &= A \exp\left(-\frac{E_a}{RT}\right) & (2) 20 \text{ L mol}^{-1} \text{ s}^{-1} &= A \exp\left(\frac{-50000 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}\right) \\ (3) 20 \text{ L mol}^{-1} \text{ s}^{-1} &= A \times 1.9699 \times 10^{-9} & (4) A &= 1.0153 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

In the Arrhenius equation (1) we know the activation energy and we must first calculate the pre-exponential factor A . Substitute the values for the variables in their base units in (2) and cancel units where possible to obtain (3) which gives us the pre-exponential factor in (4).

$$\begin{aligned} (5) k &= A \exp\left(-\frac{E_a x}{R}\right) & (6) \frac{dk}{dx} &= A \left(-\frac{E_a}{R}\right) \exp\left(-\frac{E_a x}{R}\right) & (7) \frac{dk}{dx} &= A \left(-\frac{E_a}{R}\right) \exp\left(-\frac{E_a}{RT}\right) \\ (8) \frac{dk}{dT} &= \frac{dx}{dT} \times \frac{dk}{dx} & (9) \frac{dk}{dT} &= \left(-\frac{1}{T^2}\right) A \left(-\frac{E_a}{R}\right) \exp\left(-\frac{E_a}{RT}\right) & (10) \frac{dk}{dT} &= \frac{A E_a}{R T^2} \exp\left(-\frac{E_a}{RT}\right) \end{aligned}$$

To differentiate the Arrhenius equation let $x = 1/T$ as in (5). The differential of an exponential (6) is the exponential term multiplied by any constant factor within the exponential term. In (7) substitute x with $1/T$. We use the chain rule of differentiation (8) to convert dk/dx to dk/dT as $x = T^{-1}$ then $dx/dT = -T^{-2} = -1/T^2$ to give us (9). We clean-up the equation (9) to obtain dk/dT in (10).

$$(11) \quad dk = dT \frac{AE_a}{RT^2} \exp\left(-\frac{E_a}{RT}\right)$$

$$(12) \quad dk = (1 \text{ K}) \frac{(1.0153 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1})(50000 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})^2} \exp\left(-\frac{50000 \text{ J mol}^{-1}}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}\right)$$

$$(13) \quad dk = 1.3364 \text{ L mol}^{-1} \text{ s}^{-1}$$

We separate the variables of the derivative in (10) and take dT to the right hand side to get (11). In (12) we now substitute the values for A and E_a along with $dT = 1 \text{ K}$. Equation (13) shows the change in the rate constant due to the change in temperature. As the temperature of 300 K is increased to 301 K the rate constant has increased from $20 \text{ L mol}^{-1} \text{ s}^{-1}$ to $21.3364 \text{ L mol}^{-1} \text{ s}^{-1}$ which is about a 6% increase. Those chemical and biochemical reactions which have activation energies around 50 kJ mol^{-1} are sensitive to very small ambient temperature changes.

[Return to Question 5 \(see page 104\)](#)

6.2.6 SOLUTION 6: CONSECUTIVE CHEMICAL REACTIONS

$$(1) \quad [B] = [A]_0 \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$$

$$(2) \quad \frac{d[B]}{dt} = [A]_0 \frac{k_1}{k_2 - k_1} [-k_1 \exp(-k_1 t) + k_2 \exp(-k_2 t)]$$

To calculate the maximum concentration of B we must differentiate $[B]$ with respect to t and set the derivative equal to zero. Note that for the intermediate concentration (1) of our consecutive first-order reactions the term before the square brackets is independent of time, so the differential is that of two simple exponential terms. The maximum in $[B]$ occurs when the derivative (2) $d[B]/dt$ equals zero. This would occur when either the term outside the brackets is zero (which cannot be as the initial reactant concentration and the two rate constants are non-zero) or alternatively when the term in the brackets equals zero, which gives (3) below.

$$(3) \quad k_1 \exp(-k_1 t_{\max}) = k_2 \exp(-k_2 t_{\max}) \quad (4) \quad \ln[k_1 \exp(-k_1 t_{\max})] = \ln[k_2 \exp(-k_2 t_{\max})]$$

$$(5) \quad \ln(k_1) - k_1 t_{\max} = \ln(k_2) - k_2 t_{\max} \quad (6) \quad \ln(k_1) - \ln(k_2) = k_1 t_{\max} - k_2 t_{\max}$$

$$(7) \quad \ln \frac{k_1}{k_2} = t_{\max} (k_1 - k_2) \quad (8) \quad t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

$$(9) \quad t_{\max} = \frac{1}{7 \text{ s}^{-1} - 5 \text{ s}^{-1}} \ln \frac{7 \text{ s}^{-1}}{5 \text{ s}^{-1}} \quad (10) \quad t_{\max} = 0.16824 \text{ s}$$

Take the natural logs of both sides of (3) gives (4). From (4) we use the rule of logs that the log of a product is equal to the sum of two logs, and also $\ln[\exp(x)] = x$ gives (5). (6) We rearrange (5) so that the log terms are on the left in (6) and the non-log terms are on the right. The subtraction of two log terms in (6) equals the log of the ratio of the terms (7). Rearrange (7) to (8), the time at which the intermediate is a maximum concentration depends only on the values of the two first-order rate constants, and is independent of the initial concentration of A. Substituting the values for the rate constants in (9) gives the time at which the concentration of the intermediate is a maximum (10) as 0.16824 s (the “excess” significant figures are to lessen rounding errors for section 6.2.7).

[Return to Question 6 \(see page 105\)](#)

6.2.7 SOLUTION 7: CONSECUTIVE CHEMICAL REACTIONS

It is always worth drawing graphs to be able to visualize how the algebraic equations (which may be a bit “abstract”) are modelling the chemical reactions. Also using a spreadsheet to plot the curve allows us to use non-linear curve fitting (Parker 2013, p. 33) to find the maximum of a function or where a function crosses an axis. To calculate [C] the concentration of the product we use the conservation of matter, matter is not destroyed or created in a chemical reaction, with an initial concentration $[A]_0 = 1 \text{ mol L}^{-1} = [A] + [B] + [C]$. Section 6.2.6 has the equation for $d[B]/dt$ and substituting in the values for the variables gives $d[B]/dt$ in Table 6.2.

	A	B	C	D	E	F	G	H	I	J	K	L
1 t / s	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	
2 $[A] / \text{mol L}^{-1}$	1	0.497	0.247	0.122	0.061	0.030	0.015	0.007	0.004	0.002	0.001	
3 $[B] / \text{mol L}^{-1}$	0	0.385	0.424	0.352	0.261	0.182	0.122	0.080	0.051	0.032	0.020	
4 $[C] / \text{mol L}^{-1}$	0	0.119	0.329	0.525	0.678	0.788	0.863	0.913	0.945	0.966	0.979	
5 $d[B]/dt / \text{mol L}^{-1} \text{ s}^{-1}$	7	1.552	-0.396	-0.905	-0.879	-0.697	-0.504	-0.346	-0.230	-0.149	-0.096	

Table 6.2: [A], [B], [C], and $d[B]/dt$ against time.

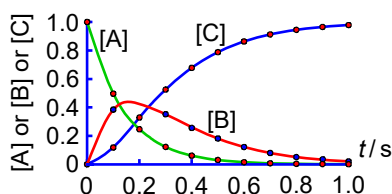


Figure 6.3: variation of [A], [B], and [C] with time.

Fig. 6.3, the reactant concentration [A] is an exponential decrease with time and initially the intermediate concentration [B] increases. As the [B] increases the rate of forming the

product [C] increases rapidly but then starts to flatten off as the [B] concentration decreases as it is being consumed and converted to [C].

Fig. 6.4 plots [B] (on a different scale to Fig. 6.3) and $d[B]/dt$ against time. When $d[B]/dt$ equals zero is the time $t_{\max} = 0.17$ s at the maximum concentration of $[B]_{\max} = 0.43$ these values agree with Section 6.2.6 (the non-linear curve fitted values are $t_{\max} = 0.16824$ s and $[B]_{\max} = 0.4312$ mol L⁻¹).

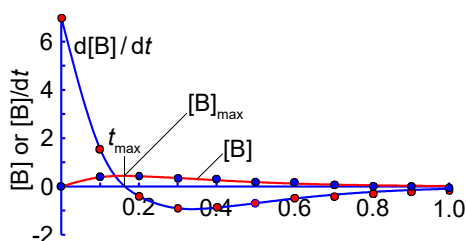


Figure 6.4: variation of [B] and $d[B]/dt$ with time.

- (1) $[B] = [A]_0 \frac{k_1}{k_2 - k_1} (\exp(-k_1 t) - \exp(-k_2 t))$
- (2) $[B]_{\max} = (1 \text{ mol L}^{-1}) \frac{7.0 \text{ s}^{-1}}{5.0 \text{ s}^{-1} - 7.0 \text{ s}^{-1}} (\exp(-7.0 \text{ s}^{-1} \times 0.16824 \text{ s}) - \exp(-5.0 \text{ s}^{-1} \times 0.16824 \text{ s}))$
- (3) $[B]_{\max} = (-3.5 \text{ mol L}^{-1})(0.3080 - 0.4312) = 0.4312 \text{ mol L}^{-1}$

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Calculating $[B]_{\max}$ from the equation for the reaction intermediate (1) we substitute $t_{\max} = 0.16824 \text{ s}$ along with $[A]_0 = 1 \text{ mol L}^{-1}$, $k_1 = 7.0 \text{ s}^{-1}$, and $k_2 = 5.0 \text{ s}^{-1}$ gives (2) and (3) and $[B]_{\max} = 0.4312 \text{ mol L}^{-1}$.

[Return to Question 7 \(see page 105\)](#)

6.2.8 SOLUTION 8: CONSECUTIVE CHEMICAL REACTIONS: THE STEADY STATE APPROXIMATION

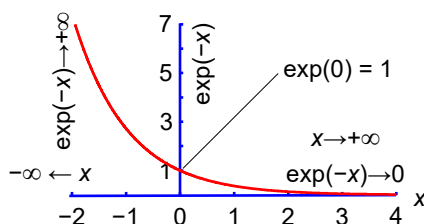


Figure 6.5: negative exponential $\exp(-x)$ versus x .

The maths involve negative exponentials and it is worth graphing the function $y = \exp(-x)$ again to show its characteristics. The negative exponential has two *asymptotes*. An asymptote is a straight line that is the limiting value of a curve, it can be considered as the tangent at infinity. The first asymptote is as x tends to plus infinity the negative exponential tends to zero. Maths symbol for “tends to the limiting value” is an arrow. The second asymptote is as x tends to minus infinity then the negative exponential tends to plus infinity. A negative exponential crosses the y -axis at $y = 1$, the y -intercept has Cartesian coordinates of $(0,1)$.

If k_1 is much smaller than k_2 ($k_1 \ll k_2$) then the following approximations may be made. As k_2 is dominantly large then $\exp(-k_2 t) \approx 0$ and as k_1 is small and *positive* then $\exp(-k_1 t) \approx \exp(0) \approx 1$. Finally $(k_2 - k_1) \approx k_2$.

$$\begin{aligned}
 (1) \quad [B] &= \frac{[A]_0 k_1}{k_2 - k_1} (\exp(-k_1 t) - \exp(-k_2 t)) & (2) \quad [B] &\approx \frac{[A]_0 k_1}{k_2} \\
 (3) \quad \frac{d[B]}{dt} &= \frac{[A]_0 k_1}{k_2 - k_1} (-k_1 \exp(-k_1 t) + k_2 \exp(-k_2 t)) & (4) \quad \frac{d[B]}{dt} &\approx -\frac{[A]_0 k_1^2}{k_2}
 \end{aligned}$$

Inserting these three approximations $\exp(-k_2 t) \approx 0$, $\exp(-k_1 t) \approx 1$, and $(k_2 - k_1) \approx k_2$ into the intermediate concentration (1) gives us (2) the approximate expression for $[B]$ when $k_1 \ll k_2$. As k_1/k_2 is a small number the intermediate concentration $[B]$ is *small* compared to $[A]_0$.

We use the same three approximations $\exp(-k_2 t) \approx 0$, $\exp(-k_1 t) \approx 1$, and $(k_2 - k_1) \approx k_2$ and substitute them into the rate of formation of the intermediate (3) gives us (4) the approximate

expression for $d[B]/dt$ when $k_1 \ll k_2$. As k_1/k_2 is a small number then k_1^2/k_2 is a *smaller* number and thus the rate $d[B]/dt$ is very small, $[B]$ is *relatively* constant compared with the initial concentration of $[A]_0$. Thus the intermediate concentration $[B]$ is both small and relatively constant compared with $[A]_0$ under the approximations where $k_1 \ll k_2$ and this is called the “steady state approximation” in chemical kinetics. The steady state approximation corresponds to where there is a relatively slow reaction k_1 forming the intermediate followed by a fast reaction k_2 of the intermediate to form the product, Fig. 6.6.

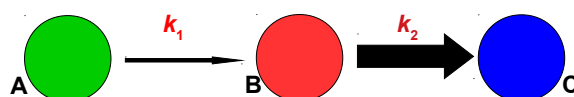


Figure 6.6: steady state approximation.

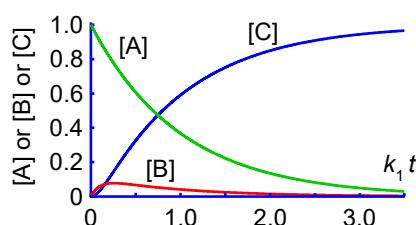


Figure 6.7: $[A]$ or $[B]$ or $[C]$ versus $k_1 t$ for $k_1 = 0.1k_2$.

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In Fig. 6.7 the concentrations are plotted against $k_1 t$ which is a dimensionless variable for first-order reactions. The steady state approximation does *not* assume the reaction intermediate concentration to be constant nor that its time derivative is zero. The steady state approximation *assumes* that the concentration of the intermediate is *near-constant* over the middle part of the reaction time frame after the initial “induction period” (where [B] increases from zero to just past its maximum value). The concentration of the intermediate is so low that even a large relative variation in its concentration is small if compared on an absolute quantitative basis against those of the reactant and product concentrations.

[Return to Question 8 \(see page 105\)](#)

6.2.9 SOLUTION 9: CONSECUTIVE CHEMICAL REACTIONS WITH A RATE DETERMINING STEP

When $k_1 \gg k_2$ (the opposite conditions from section 6.2.8) then the following approximations may be made from Fig. 6.5 for the properties of negative exponential functions. The condition $k_1 \gg k_2$ means $\exp(-k_1 t) \approx 0$ and as k_2 is small and *positive* then $\exp(-k_2 t) \approx \exp(0) \approx 1$ and $(k_2 - k_1) \approx -k_1$.

$$\begin{aligned} (1) \quad [B] &= \frac{[A]_0 k_1}{k_2 - k_1} (\exp(-k_1 t) - \exp(-k_2 t)) & (2) \quad [B] &\approx [A]_0 \\ (3) \quad \frac{d[B]}{dt} &= \frac{[A]_0 k_1}{k_2 - k_1} (-k_1 \exp(-k_1 t) + k_2 \exp(-k_2 t)) & (4) \quad \frac{d[B]}{dt} &\approx -[A]_0 k_2 \end{aligned}$$

Inserting these three approximations $\exp(-k_1 t) \approx 0$, $\exp(-k_2 t) \approx 1$, and $(k_2 - k_1) \approx -k_1$ into the intermediate concentration (1) gives us the approximate expression (2) for $[B] \approx [A]_0$ when $k_1 \gg k_2$. The concentration of the intermediate is of the same order of magnitude as the *initial* concentration of the reactant.

We use the same approximations $\exp(-k_1 t) \approx 0$, $\exp(-k_2 t) \approx 1$, and $(k_2 - k_1) \approx -k_1$ and substitute into the rate of forming the intermediate $d[B]/dt$ (3) which gives (4). From (4), after the induction period when [B] is a maximum, for the rest of the reaction time the rate of *loss* of the intermediate to form the product is approximately $-d[B]/dt \approx [A]_0 k_2$. But from (2) this is the same as $-d[B]/dt \approx [B] k_2$ that is the rate of formation of the product is approximately the rate of the slow second step $B \rightarrow C$ of the consecutive reactions and is approximately independent of the rate of the fast first step $A \rightarrow B$. This second step is a reaction “bottle neck” and is called the “rate determining step”, Fig. 6.8.

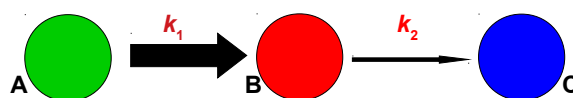


Figure 6.8: rate determining step.

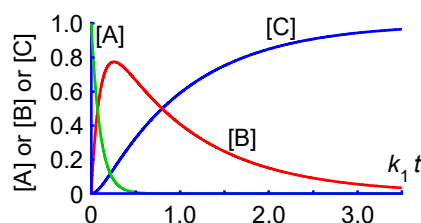


Figure 6.9: [A], [B], and [C] versus $k_1 t$ for $k_1 = 10k_2$.

Fig. 6.9 the relatively large value of k_1 causes the [A] reactant concentration to decrease rapidly and a large concentration of the intermediate [B] to be quickly formed. The product concentration [C] does not start to appreciably increase until the intermediate concentration [B] has passed its maximum by which time the reactant concentration [A] is negligible. That is the formation of the product C is approximately determined by the large intermediate concentration [B] with a $B \rightarrow C$ rate determining step.

[Return to Question 9 \(see page 106\)](#)

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 of a derivative” method for integrating a differential equation.

7.1 WEEK 7 TUTORIAL QUESTIONS

7.1.1 QUESTION 1: RADIOACTIVE DECAY

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

$$\frac{d[A]}{dt} = -k[A] \quad \text{Rate of reaction for radioactive decay}$$

The rate of reaction is equal to the product of the rate constant k and the concentration $[A]$ of the reactant at that particular time. The negative sign is to give a *positive* rate constant for the reaction which involves the *loss* of the reactant. In order to calculate the concentration of A remaining at time t we need to integrate this equation from $t = 0$ at which $[A] = [A]_0$ to a general time $t = t$ where $[A] = [A]_t$. Carry out this definite integration for this first-order chemical radioactive decay reaction.

[Jump to Solution 1 \(see page 120\)](#)

7.1.2 QUESTION 2: SECOND-ORDER CHEMICAL REACTIONS

We have looked at chemical reactions with first-order reaction rate laws, another common type is a second-order rate law. This may occur in two forms depending upon whether there are one or two species of reactant molecule.

$$(1) \frac{d[A]}{dt} = \overbrace{-k[A]^2}^{A \rightarrow P} \quad (2) \frac{d[A]}{dt} = \overbrace{-k[A][B]}^{A+B \rightarrow P} \quad \text{Definition: second-order rate laws}$$

An example of a second-order reaction is the decomposition of nitrogen dioxide at around 150 °C with the stoichiometric equation $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$.

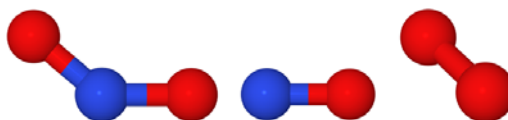


Figure 7.1: NO_2 , NO , and O_2 with N (blue) and O (red).

NO_2 (brown gas) is involved in important chemical reactions in polluted atmospheres and also in the industrial manufacture of nitric acid and hence nitrates. The rate of loss of NO_2 is expressed by the second-order rate law below.

$$-\frac{d[\text{NO}_2]}{dt} = k[\text{NO}_2]^2$$

The fact that the reaction is second-order and the stoichiometric coefficient of NO_2 is also 2 is purely a coincidence and does *not* imply anything about the mechanism of reaction. To calculate the concentration of NO_2 at any time during this reaction we need to integrate this

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equation from $t = 0$ where $[\text{NO}_2] = [\text{NO}_2]_0$ to a general time $t = t$ when $[\text{NO}_2] = [\text{NO}_2]_t$. Carry out this definite integration for this second-order chemical reaction.

[Jump to Solution 2 \(see page 122\)](#)

7.1.3 QUESTION 3: EXPANDING GAS AND THERMODYNAMIC WORK

In chemistry it is very common to have gases involved in reactions, they may be formed, or react, or be compressed, or expand. A simple way of understanding such processes is to begin with a “mechanical” picture of a gas trapped inside a cylinder by a movable piston.



Figure 7.2: expansion of a gas of volume V and pressure p_{ex} .

In thermodynamics the material we are investigating (gas in this case) is called the “system” and everything other than the system is called the “surroundings”. The system plus the surroundings is called the “universe”. If the external pressure of the surroundings is p_{ex} and the gas in our “gas piston” is always kept at the same pressure of the external surroundings by supplying heat as the volume increases it is called a “reversible expansion”. If the initial volume of the system is V_i the pressure-volume work (p - V) done *on* the gas (w) in *expanding* the gas to a final volume V_f is given by the integral below and Fig. 7.3 (left).

$$w = - \int_{V_i}^{V_f} p_{\text{ex}} dV$$

Work done *on* the system by a reversible expansion

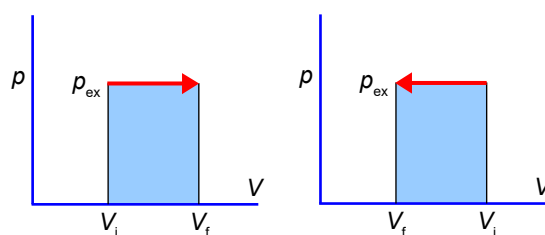


Figure 7.3: reversible expansion of a gas (left), and reversible compression (right).

In Fig. 7.3 (left) starting at p_{ex} and V_i we heat the gas to keep the pressure constant and increase the volume to V_f the gas follows the red line and the work done on the gas is equal to *minus* the area under the p - V curve, called the *line integral* of the p - V plot. The sign convention is that work done *on* the gas by expansion the gas is negative, the system (gas) has done work in pushing the surroundings backwards out of the way. The work done *on* the system (gas) in compression Fig. 7.3 (right) is plus the area under the line, the system

follows the red line and has decreased its volume by the surroundings pushing the gas into a smaller volume and the gas losing heat in order to maintain constant pressure.

Assuming the gas is an ideal gas, calculate the work done when the gas expands from an initial volume V_i to a final volume V_f by integrating the p - V work equation.

[Jump to Solution 3 \(see page 123\)](#)

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 $T = 298 \text{ K}$ in a thermostated bath. Using your solution from section 7.2.3 calculate the work done on the gas in this expansion.

[Jump to Solution 4 \(see page 123\)](#)

7.2 WEEK 7 TUTORIAL SOLUTIONS

7.2.1 SOLUTION 1: RADIOACTIVE DECAY

$$\int \frac{1}{x} dx = \ln(x) \quad \text{Standard integral of a reciprocal of a variable}$$

Where C is the constant of integration. Using this solution I am going to introduce the “separation of the variables of a derivative” method for integrating a function.

$$\begin{aligned} (1) \quad \frac{d[A]}{dt} &= -k[A] & (2) \quad \frac{d[A]}{[A]} &= -k dt \\ (3) \quad \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} &= -k \int_0^t dt & (4) \quad [\ln[A] + C]_{[A]_0}^{[A]_t} &= -k[t]_0^t \end{aligned}$$

(1) Treat the derivative $d[A]/dt$ as two separate variables $d[A]$ and dt each of which follow the normal rules of algebra. Importantly you *cannot* separate “d” an operator, from “t” the operand (a variable which is operated on), as the operator “d” has to operate on its operand. Similarly with any other operator-variable combination such as $d[A]$. Rearrange equation (1) to bring everything that involves $[A]$ to the left hand side and everything that involves t or are constants or a minus sign to the right hand side of equation (2). Integrate both sides of the equation (3) separately, using the two sets of appropriate integration limits,

be careful to check these limits! Take any constants and the negative sign outside of the integral for clarity, note the rate constant k is independent of time and is constant. Both the left and right hand sides of the equation are standard integrals. The left hand side making use of the standard integral of a reciprocal. Evaluating the definite integral (4) will cancel out the constant of integration. This gives us four equivalent ways of writing the definite integral, which one we choose to use to solve a particular problem will depend upon the circumstances.

$$\ln[A]_t - \ln[A]_0 = -k t \quad \ln \frac{[A]_t}{[A]_0} = -k t$$

$$\frac{[A]_t}{[A]_0} = \exp(-k t) \quad [A]_t = [A]_0 \exp(-k t)$$

Integrated first-order rate law

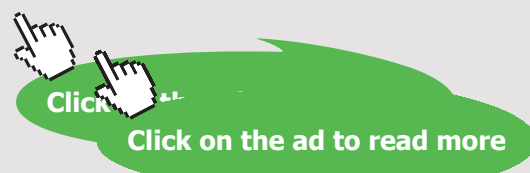
[Return to Question 1 \(see page 117\)](#)



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7.2.2 SOLUTION 2: SECOND-ORDER CHEMICAL REACTIONS

We have integrated first-order rate laws above but what about second-order chemical kinetic rate laws?

$$\begin{aligned}
 (1) \quad \frac{d[A]}{dt} &= -k[A]^2 & (2) \quad \frac{d[A]}{[A]^2} &= -k dt & (3) \quad \int_{[A]_0}^{[A]_t} [A]^{-2} d[A] &= -k \int_0^t dt \\
 (4) \quad \left[\frac{[A]^{-1}}{-1} + C \right]_{[A]_0}^{[A]_t} &= -k[t]_0^t & (5) \quad \left[-\frac{1}{[A]} + C \right]_{[A]_0}^{[A]_t} &= -k t & (6) \quad -\frac{1}{[A]_t} - \left(-\frac{1}{[A]_0} \right) &= -k t
 \end{aligned}$$

To make the solution a general one, in (1) let's replace NO_2 by A for the integration. We use the method of "separation of variables" for the integration of this second order rate law. Treat " $d[A]$ " and " dt " as separate variables and bring everything that involves $[A]$ to the left hand side and everything that involves t or is a constant or a minus sign to the right hand side of (2). Now in (3) integrate both sides separately with the appropriate limits. An easy and foolproof way of integrating the left hand side of the equation is to write it as $[A]^{-2}$ and then integrate as normal. You can use this "trick" to integrate many equations which at first sight might look a bit difficult. In (5) write $[A]^{-1}$ as $1/[A]$. Evaluate the definite integral (6) and the constant of integration cancels. Multiply (6) by minus throughout to obtain the integrated second-order rate law with one reactant species as shown below.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k t \quad \text{Integrated second-order rate law with one reactant}$$

For the specific example of the nitrogen dioxide decomposition this corresponds to the following.

$$\frac{1}{[\text{NO}_2]_t} - \frac{1}{[\text{NO}_2]_0} = k t$$

[Return to Question 2 \(see page 117\)](#)

7.2.3 SOLUTION 3: EXPANDING GAS AND THERMODYNAMIC WORK

$$\begin{aligned}
 (1) \quad pV &= nRT & (2) \quad p &= \frac{nRT}{V} & (3) \quad w &= - \int_{V_i}^{V_f} p_{\text{ex}} dV \\
 (4) \quad w &= - \int_{V_i}^{V_f} \frac{nRT}{V} dV & (5) \quad w &= -nRT \int_{V_i}^{V_f} \frac{1}{V} dV & (6) \quad w &= -nRT [\ln V]_{V_i}^{V_f} \\
 (7) \quad w &= -nRT (\ln V_f - \ln V_i)
 \end{aligned}$$

The ideal gas law (1) gives us the pressure of the gas in (2) which we substitute into the pressure-volume work equation (3) to obtain (4). Take the constants outside the integral (5) and integrate using the standard integral of a reciprocal $\int dx/x = \ln x$ to (6) and evaluate the integral between its two limits (7). Finally write the difference of two log terms as the log of the ratio of the two terms.

$$w = -nRT \ln \frac{V_f}{V_i} \quad p\text{-}V \text{ work done on the system in an ideal gas expansion}$$

[Return to Question 3 \(see page 119\)](#)

7.2.4 SOLUTION 4: IDEAL GAS EXPANSION

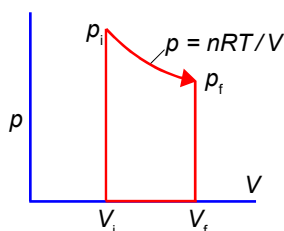


Figure 7.4: isothermal reversible expansion of an ideal gas.

$$\begin{aligned} (1) \quad w &= -nRT \ln \frac{V_f}{V_i} & (2) \quad w &= -(1 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln \frac{2.45 \times 10^4 \text{ cm}^3}{4.90 \times 10^3 \text{ cm}^3} \\ (3) \quad w &= -3.99 \times 10^3 \text{ J} & (4) \quad w &= -3.99 \text{ kJ} \end{aligned}$$

Isothermal just means the change takes place at constant temperature. The work done on the ideal gas is the area under the curved arrow between the two limits of volume in equation (1). Substituting the values for physical quantities in (2). Quote the work done on the gas (4) in the conventional multiples of kilojoules -3.99 kJ . The gas is doing work on the surroundings in the isothermal reversible expansion process as the gas is “pushing back” the surroundings.

[Return to Question 4 \(see page 120\)](#)

8 WEEK 8: CHEMISTRY AND INTEGRATION 2

8.1 WEEK 8 TUTORIAL QUESTIONS

8.1.1 QUESTION 1: HEAT CAPACITY OF A MOLECULE AND TEMPERATURE CHANGES

NASA has fitted high quality experimental data for the standard heat capacity at constant pressure C_p° (also called the isobaric heat capacity), the standard enthalpy H° , and the standard entropy S° for more than 2000 solid, liquid and gaseous chemical species over an extremely wide temperature range to three polynomial equations called the NASA polynomials (McBride *et al*, 2002). The polynomial equations are shown below in a dimensionless form where R is the gas constant, and b_1 and b_2 are constants of integration. The polynomials each have seven-terms with temperature raised to the powers running from -2 to $+4$ and they are designed for easy computer manipulation of the data.

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$$\begin{aligned}\frac{C_p^\circ}{R} &= a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4 \\ \frac{H^\circ}{RT} &= -a_1 T^{-2} + a_2 \frac{\ln(T)}{T} + a_3 + a_4 \frac{T}{2} + a_5 \frac{T^2}{3} + a_6 \frac{T^3}{4} + a_7 \frac{T^4}{5} + \frac{b_1}{T} \\ \frac{S^\circ}{R} &= -a_1 \frac{T^{-2}}{2} - a_2 T^{-1} + a_3 \ln(T) + a_4 T + a_5 \frac{T^2}{2} + a_6 \frac{T^3}{3} + a_7 \frac{T^4}{4} + b_2\end{aligned}$$

NASA polynomial equations

The polynomial equation for enthalpy is obtained by integrating C_p° with respect to T and for entropy by integrating C_p°/T with respect to T . These integrations arise from the thermodynamic definitions below.

$$C_p^\circ = \left(\frac{\partial H^\circ}{\partial T} \right)_p \rightarrow \Delta H^\circ = \int_{T_1}^{T_2} C_p^\circ dT$$

Constant pressure heat capacity and enthalpy

$$\Delta S^\circ = \frac{\Delta H^\circ}{T} \rightarrow \Delta S^\circ = \int_{T_1}^{T_2} \frac{C_p^\circ}{T} dT$$

Constant pressure heat capacity and entropy

The coefficients a_1 to a_7 for N_2 between 200 K and 1000 K are tabulated by NASA to 10 significant figures for computer manipulation. I have rounded the data to four significant figures for use with a calculator.

a_1	a_2	a_3	a_4	a_5	a_6	a_7
2.210×10^4	-3.818×10^2	6.083	-8.531×10^{-3}	1.385×10^{-5}	-9.626×10^{-9}	2.520×10^{-12}

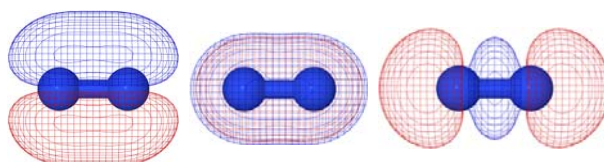


Figure 8.1: N_2 π -bond in-plane, π -bond out-of-plane, and σ -bond.

- 1) Integrate the heat capacity polynomial equation between 273 K and 373 K (0 °C to 100 °C). This integrated equation is equal to the enthalpy change $\Delta H^\circ(373-273 \text{ K})$ of nitrogen.
- 2) Substitute in the values of the coefficients for N_2 into your integrated equation to find heat capacity change between 273 K and 373 K, (the area under the curve) which is the enthalpy change $\Delta H^\circ(373-273 \text{ K})$ of N_2 for this constant-pressure temperature change.
- 3) Using a spreadsheet plot the graph of C_p° for N_2 against T at 20 K intervals between 200 and 1000 K. Calculate the enthalpy change for N_2 on heating from 273 to 373 K.

- 4) Using a spreadsheet plot the graph of C_p/T against T at 20 K intervals between 200 and 1000 K. Calculate the entropy change for N_2 on heating from 273 to 373 K.

[Jump to Solution 1 \(see page 129\)](#)

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 components or moieties of many biological molecules, *e.g.* β -carotene and lycopene.

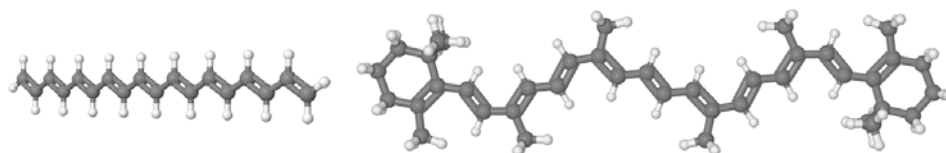


Figure 8.2: C18 linear polyene molecule (left) and β -carotene (right).

Because of the alternation of the single and double bonds, the π -electrons are *mobile* and may move along the whole length of the polyene. We may treat the polyene molecule as a “one-dimensional” box of length L which confines the mobile π -electrons. This interesting and important quantum mechanics 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 -electrons in that level.

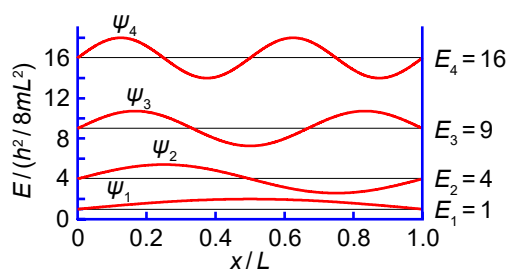


Figure 8.3: wavefunction (in red) for π -electrons in a polyene molecule.

The probability of finding a π -electron at a certain position x in the box of length L is given by integrating the square of the wavefunction (which you derived in section 2.2.10) over the length of the box.

$$\int_{x=0}^{x=L} B^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

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

$$\int \sin^2(ax) dx = \frac{x}{2} - \frac{1}{4a} \sin(2ax) + C$$
 Standard integral for a sine squared function

[Jump to Solution 2 \(see page 131\)](#)

8.1.3 QUESTION 3: THE 1s ELECTRON OF THE HYDROGEN ATOM

The radial distribution function $P(r)$ is the probability density that the electron is in a thin spherical shell which is a distance r from the nucleus and thickness dr . The H-atom 1s electron radial distribution function is shown below.

$$P(r) = \frac{4}{a_0^3} r^2 \exp\left(-\frac{2r}{a_0}\right)$$
 Radial distribution function for a 1s electron of a H-atom

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Where a_0 is a constant called the Bohr radius ($a_0 = 0.5292 \text{ \AA}$ or $a_0 = 0.5292 \times 10^{-10} \text{ m}$). Fig. 8.4 plots the hydrogen atom 1s electron radial distribution function. The maximum in Fig. 8.4 is at the Bohr radius.

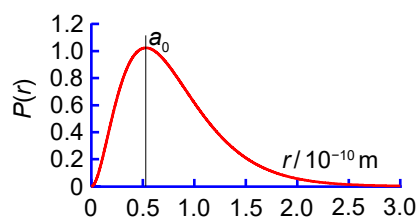


Figure 8.4: H-atom 1s electron radial distribution function.

Calculate the probability of finding the electron at a radius of *less* than $2a_0$, that is integrate the 1s H-atom radial distribution function from $r = 0$ to $r = 2a_0$. Note that $4/a_0^3$ is a constant and may be taken outside the integral.

$$\text{Probability} = \frac{4}{a_0^3} \int_0^{2a_0} r^2 \exp\left(-\frac{2r}{a_0}\right) dr$$

We need to integrate the product of two function of r . We will integrate $\int uv \, dx$ using the “integration by parts tabular method” with $u = x^2$ and $v = \exp(bx)$ ($x = r$ and $b = -2/a_0$) and we set up the table below with each row the differential of the term above or the integral of the term above.

A	B
du/dx	$\int v \, dx$
x^2	$\exp(bx)$
$2x$	$\frac{1}{b} \exp(bx)$
2	$\frac{1}{b^2} \exp(bx)$
0	$\frac{1}{b^3} \exp(bx)$

Integration by parts, tabular method

We pair the first entry of column A with the second entry of column B; then the second entry of column A with the third entry of column B, *etc.* alternating the signs starting with a positive sign and carry on until the product of the pairing is zero.

$$\begin{aligned} \int x^2 \exp(bx) \, dx &= (+)(x^2) \left(\frac{1}{b} \exp(bx) \right) (-)(2x) \left(\frac{1}{b^2} \exp(bx) \right) (+)(2) \left(\frac{1}{b^3} \exp(bx) \right) + C \\ \int x^2 \exp(bx) \, dx &= \frac{x^2}{b} \exp(bx) - \frac{2x}{b^2} \exp(bx) + \frac{2}{b^3} \exp(bx) + C \\ \int x^2 \exp(bx) \, dx &= \exp(bx) \left(\frac{x^2}{b} - \frac{2x}{b^2} + \frac{2}{b^3} \right) + C \end{aligned}$$

[Jump to Solution 3 \(see page 132\)](#)

8.2 WEEK 8 TUTORIAL SOLUTIONS

8.2.1 SOLUTION 1: ENTHALPY OF A MOLECULE AND TEMPERATURE CHANGES

The integral from 273 K to 373 K is shown below where $\Delta H^\circ(373 \text{ K} - 273 \text{ K})$ is written as ΔH° for brevity.

$$\begin{aligned}
 (1) \quad \Delta H^\circ / R &= \int_{273\text{K}}^{373\text{K}} a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4 dT \\
 (2) \quad \Delta H^\circ / R &= \left[-a_1 T^{-1} + a_2 \ln T + a_3 T + a_4 T^2/2 + a_5 T^3/3 + a_6 T^4/4 + a_7 T^5/5 + C \right]_{273\text{K}}^{373\text{K}} \\
 (3) \quad \Delta H^\circ / R &= -a_1(1/373 - 1/273) + a_2 \ln(373/273) + a_3(100) + a_4(373^2 - 273^2)/2 \\
 &\quad + a_5(373^3 - 273^3)/3 + a_6(373^4 - 273^4)/4 + a_7(373^5 - 273^5)/5
 \end{aligned}$$

Notice that the constant of integration in (2) has cancelled out in the definite integral (3). Each of the terms in the definite integral (3) has units of kelvin which are not shown for clarity. We now substitute the values of the NASA polynomial coefficients a_1 to a_7 for N_2 .

$$\begin{aligned}
 (4) \quad \Delta H^\circ / R &= -(2.210 \times 10^4)(-9.820 \times 10^{-4}) + (-3.818 \times 10^2)(0.3121) + (6.083)(100) \\
 &\quad + (-8.531 \times 10^{-3})(6.46 \times 10^4)/2 + (1.385 \times 10^{-5})(3.155 \times 10^7)/3 \\
 &\quad + (-9.626 \times 10^{-9})(1.380 \times 10^{10})/4 + (2.520 \times 10^{-12})(5.704 \times 10^{12})/5 \\
 (5) \quad \Delta H^\circ / R &= 21.70 - 119.2 + 608.3 - 275.6 + 145.7 - 33.21 + 2.875 = 350.6 \text{ K} \\
 (6) \quad \Delta H^\circ(373 \text{ K} - 273 \text{ K}) &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(350.6 \text{ K}) = 2.915 \text{ kJ mol}^{-1}
 \end{aligned}$$

The enthalpy change in heating N_2 from 0 °C to 100 °C is $\Delta H^\circ(373 - 273 \text{ K}) = 2.915 \text{ kJ mol}^{-1}$ to four significant figures. As well as the above integration by hand method we can use a spreadsheet to manipulate this type of data.

	A	B	C	D	E
	coefficients	T/K	C_p° / R	$C_p^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	$(C_p^\circ / T) / (\text{J K}^{-2} \text{ mol}^{-1})$
1					
2	2.210E+04	200	3.5008010981844	29.1056603303051	0.145528301651526
3	-3.818E+02	220	3.50053691904025	29.1034639449007	0.132288472476821
4	6.083E+00	240	3.50088720783515	29.1063762459415	0.121276567691423
5	-8.531E-03	260	3.50139180987875	29.1105715073319	0.111963736566661
6	1.385E-05	280	3.50202581440488	29.1158426209622	0.103985152217722
7	-9.626E-09	300	3.50293502274623	29.1234017791122	0.097078005930374
8	2.520E-12	320	3.50431374413353	29.1348644687261	0.091046451464769
9		340	3.50634959958784	29.1517905709733	0.085740560502863
10		360	3.50920050549128	29.1754930026545	0.081043036118485

Table 8.1: part of the spreadsheet for heat capacity plots.

Table 8.1 is the top-left corner of the spreadsheet with A2 to A8 the polynomial coefficients for N_2 typed manually. The temperatures B2 to B10 were typed in manually. Cells B2 to B10 were selected with the mouse, and the right-bottom handle was pulled down to dynamically copy the selection to B42 to give the temperature range 200-1000 K in steps

of 20 K and the selection handle was released. The formulae C3 to E3 were manually typed, C2 is $C_p^\circ/R = (A\$2*B2^{-2})+(A\$3*B2^{-1})+A\$4+(A\$5*B2^1)+(A\$6*B2^2)+(A\$7*B2^3)+(A\$8*B2^4)$, D2 is $C_p^\circ/(J\ K^{-1}\ mol^{-1}) = 8.314*C2$, and E2 is $(C_p^\circ/T)/(J\ K^{-2}\ mol^{-1}) = D2/B2$. These three formulae are selected and the right-bottom handle of the selection is dragged down to dynamically copy down to E42 and then the selection handle is released.

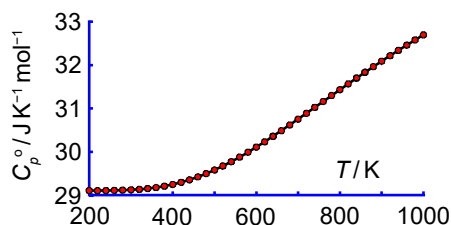


Figure 8.5: N_2 plot of C_p versus T .

Fig. 8.5 is the spreadsheet plot of the heat capacity C_p° against temperature. Integration of Fig. 8.5 from 273 to 373 K, (the area under the curve) obtained by using a spreadsheet is $\Delta H^\circ(373-273\ K) = 2.914\ kJ\ mol^{-1}$ which agrees to within three figures with the direct integration. Calculating an area under a curve is best accomplished using Graph 4.4.2 (Johansen, 2013).

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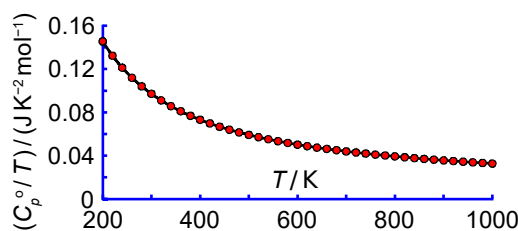


Figure 8.6: N₂ C_p/T versus T.

In Fig. 8.6 the heat capacity divided by the temperature C_p^o/T is plotted against the temperature T . The area under the curve, the integral, between any two temperatures is the entropy change between these temperatures $\Delta S^o(T_2-T_1)$, and between 273 and 373 K it is $\Delta S^o(373-273) = 9.0903 \text{ J K}^{-1} \text{ mol}^{-1}$.

The thermodynamic quantity most “easily” experimentally measured is the heat capacity which is the amount of heat (usually supplied as electrical energy) needed to increase the temperature by one degree Celsius or one kelvin. Once C_p^o is measured using an adiabatic constant-pressure calorimeter at different temperatures we can graphically find the enthalpy and the entropy of the system, as above.

[Return to Question 1 \(see page 124\)](#)

8.2.2 SOLUTION 2: QUANTUM MECHANICS OF A CONJUGATED POLYENE MOLECULE

$$\begin{aligned}
 (1) \quad & B^2 \left[\frac{L}{2} - \overbrace{\frac{L}{4n\pi} \sin(2n\pi)}^{=0} \right] - B^2 \left[\frac{0}{2} - \overbrace{\frac{0}{4n\pi} \sin(0)}^{=0} \right] = 1 \\
 (2) \quad & B^2 \frac{L}{2} = 1 \quad B^2 = \frac{2}{L} \quad B = \sqrt{\frac{2}{L}}
 \end{aligned}$$

Let us write $a = n\pi/L$ and then the integral of the wavefunction squared is $B^2 \int \sin^2(ax) dx$ for a particle in a box. In (1) we use the standard integral $B^2 \int \sin^2(ax) dx = B^2 [x/2 - (1/4a) \sin(2ax) + C]$ between the limits of x equals 0 and L . This definite integral is equal to unity, the total probability for the mobile π -electrons trapped in the polyene. The term $\sin(2n\pi)$ in (1) 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) so the lower limit is zero also the second term of the upper limit is zero. The constant B is called the normalization constant as it makes the total probability of our π -electron being located in the polyene equal to unity,

we have normalized the probability. 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.

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

Wavefunctions for a particle in a one-dimensional box

[Return to Question 2 \(see page 126\)](#)

8.2.3 SOLUTION 3: THE 1s ELECTRON OF THE HYDROGEN ATOM

$$\begin{aligned} (1) \text{ probability} &= \frac{4}{a_0^3} \left[\exp\left(-\frac{2r}{a_0}\right) \left(-\frac{a_0 r^2}{2} - \frac{2a_0^2 r}{2^2} - \frac{2a_0^3}{2^3} \right) + C \right]_{r=0}^{r=2a_0} \\ (2) \text{ probability} &= \frac{4}{a_0^3} \left[\exp(-4) \left(-2a_0^3 - a_0^3 - \frac{a_0^3}{4} \right) - \exp(-0) \left(-0 - 0 - \frac{a_0^3}{4} \right) \right] \\ (3) \text{ probability} &= \frac{4}{a_0^3} \exp(-4) \left(-\frac{13a_0^3}{4} \right) - \frac{4}{a_0^3} \left(-\frac{a_0^3}{4} \right) = -13 \exp(-4) + 1 = 0.7619 \end{aligned}$$

We are calculating the integral of the radial distribution function between r equals 0 and $2a_0$ using the integration by parts by the tabular method explained in the section 8.1.3. Substitute in (2) the two limits for our integral and the integration constant cancels out. (3) The probability of the electron being between $2a_0$ and 0 from the nucleus for the 1s atomic orbital of a H-atom is 0.7619. 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 which has an asymptote at a radius of infinity and Fig. 8.7 for the 3-dimensional 1s atomic orbital drawn to enclose 90% of the total probability.

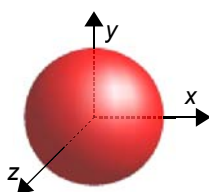


Figure 8.7: 1s atomic orbital.

[Return to Question 3 \(see page 127\)](#)

Postscript

This workbook is the first of three books which continue with *Intermediate Maths for Chemists* (Parker 2012) and *Advanced Maths for Chemists* (Parker 2013). The three books together cover a typical first year maths course for your chemistry or related science or

engineering degree. Also the three books are very useful for *future reference* in later years of your degree(s). Go to my web page for links to download the other two maths books and also books on quantum mechanics and spectroscopy.

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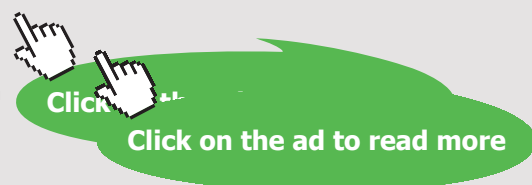
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10 LIST OF FORMULAE

The formulae in order of appearance.

$$\underbrace{c}_{\text{physical quantity}} = \underbrace{2.9979 \times 10^8}_{\text{pure number}} \underbrace{\text{m s}^{-1}}_{\text{units}} \quad \text{Definition: a physical quantity}$$

$$y = mx + c \quad \text{Equation of a linear graph}$$

$$\begin{array}{ll} (1) \ 5 = m2 + c & (2) \ 14 = m8 + c \\ (3) \ 9 = m6 & m = 1.5 \quad (4) \ 19 = m10 + 2c \\ (5) \ 19 = 1.5 \times 10 + 2c & c = 2 \quad (6) \ y = 1.5x + 2.0 \end{array} \quad \text{Finding the equation of a linear graph}$$

$$c = \lambda \nu \quad \text{Wavelength and frequency of light}$$

$$c = \frac{n}{V} \quad \text{Definition: concentration in mol L}^{-1}$$

$$\begin{array}{ll} c_A = [A] \text{ mol L}^{-1} & c_B = [B] \text{ mol L}^{-1} \\ c_C = [C] \text{ mol L}^{-1} & c_D = [D] \text{ mol L}^{-1} \end{array} \quad \text{Molar concentration}$$

$$K_c^\circ = \frac{[C]^3 [D]^2}{[A] [B]^2} \quad \text{Standard concentration equilibrium constant, a pure number}$$

$$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{HBr}(\text{g}) \quad \nu = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]} \quad \begin{array}{l} \text{Stoichiometric equation and} \\ \text{rate law} \end{array}$$

$$p = \frac{nRT}{V-nb} - \frac{an^2}{V^2} \quad \left(p + \frac{an^2}{V^2} \right) (V-nb) = nRT \quad \text{Two versions of the van der Waals equation}$$

$$\frac{d \ln p}{dT} \approx \frac{\Delta_{\text{vap}} H^\circ}{RT^2} \quad \text{Clausius-Clapeyron equation}$$

$$\binom{n}{k} = \frac{n!}{k!(n-k)!} \quad \text{Definition: binomial theorem}$$

$$n! = n(n-1)(n-2)(n-3) \cdots 1 \quad \text{Definition: the factorial of } n$$

$$\begin{array}{ccccccc} & & & & 1 & & \\ & & & 1 & & 1 & \\ & 1 & & 2 & & 1 & \\ 1 & & 3 & & 3 & & 1 \\ 1 & & 4 & & 6 & & 4 & & 1 \\ 1 & & 5 & & 10 & & 10 & & 5 & & 1 \end{array} \quad \text{Pascal's triangle of binomial coefficients}$$

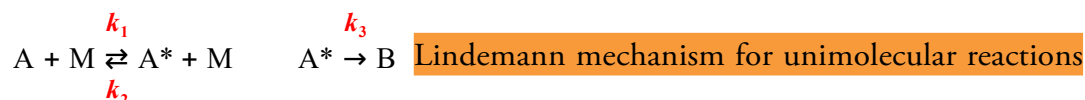
$$\left(\frac{\partial p}{\partial V_m} \right)_T = 0 \quad \left(\frac{\partial^2 p}{\partial V_m^2} \right)_T = 0 \quad \text{Point of inflection in a curve of } p = f(V_m)$$

$$a = \frac{27 R^2 T_c^2}{64 p_c} \quad b = \frac{RT_c}{8 p_c} \quad \text{The van der Waals parameters from experimental } p_c \text{ and } T_c$$

$$\frac{1}{(a_0 - x)(b_0 - x)} \equiv \frac{A}{(a_0 - x)} + \frac{B}{(b_0 - x)} \quad \text{Definition: partial fraction}$$

$$E = h\nu \quad \text{Photon energy}$$

$$\Delta_{\text{lat}} H^\circ = -\Delta_f H^\circ + \Delta_{\text{sub}} H^\circ + \frac{1}{2} \Delta H^\circ(\text{Cl-Cl}) + \Delta_{\text{ion}} H^\circ + \Delta_{\text{eg}} H^\circ \quad \text{KCl Born-Haber cycle}$$



$$\Delta_r H^\circ = \sum n_i \Delta_f H^\circ(\text{products}) - \sum n_i \Delta_f H^\circ(\text{reactants}) \quad \text{Definition: standard reaction enthalpy}$$

$$\bar{\nu} \text{ cm}^{-1} = \frac{1}{\lambda \text{ cm}} \quad \text{Definition: wavenumber}$$

$$\bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{Rydberg equation for H-atom electronic spectra}$$

$$2d \sin \theta = n\lambda \quad n = 1, 2, 3, \dots \quad \text{The Bragg equation for X-ray diffraction}$$

$$\langle r^2 \rangle = Nl^2 \frac{1 - \cos \theta}{1 + \cos \theta} \quad \text{Average end-to-end distance } \langle r \rangle \text{ of an ideal random coil polymer}$$

$$\psi(x) = A \cos(kx) + B \sin(kx) \quad \text{General wavefunction that applies to all wave motion}$$

$$K_a = \frac{[\text{CH}_2\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{Acetic acid acidity constant } K_a$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \text{The quadratic formula}$$

$$K_p^\circ = \frac{[p(\text{NH}_3)_{\text{eq}}/p^\circ]^2}{[p(\text{N}_2)_{\text{eq}}/p^\circ][p(\text{H}_2)_{\text{eq}}/p^\circ]^3} \quad \text{Ammonia standard pressure equilibrium constant}$$

$$v \approx \frac{k_3 k_1}{k_2} [\text{A}] \quad \text{Lindemann rate of "unimolecular" isomerization reactions}$$

$$(1) \log_b(x \times y) = \log_b(x) + \log_b(y)$$

$$(2) \log_b\left(\frac{x}{y}\right) = \log_b(x) - \log_b(y) \quad \text{Rules of logs}$$

$$(3) \log_b(x^n) = n \log_b(x)$$

$$(1) \log_b(b) = 1 \quad (2) \log_b(b)^x = x$$

$$(3) b^{\log_b(x)} = x \quad (4) \log_b(a) = \frac{1}{\log_a(b)} \quad \text{Additional rules of logs}$$

$$e = \lim_{n \rightarrow \infty} \left(1 + \frac{1}{n}\right)^n = \overbrace{1}^{n=0} \overbrace{2}^{n=1} \overbrace{2.25}^{n=2} \overbrace{2.488}^{n=5} \overbrace{2.593}^{n=10} \overbrace{2.704}^{n=100} \overbrace{2.716}^{n=1000} \overbrace{2.718}^{n=10000} \overbrace{\dots}^{n=\dots}$$

Euler's number

$$e = \sum_{n=0}^{\infty} \frac{1}{n!} = \frac{1}{0!} + \frac{1}{1!} + \frac{1}{1!} + \frac{1}{3!} + \frac{1}{4!} + \frac{1}{5!} + \frac{1}{6!} + \frac{1}{7!} + \frac{1}{8!} + \frac{1}{9!} + \frac{1}{10!} + \dots \approx 2.718$$

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

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

Euler's number raised to the powers x and $-x$

$$(1) \log_b(a) = \frac{\log_b(x)}{\log_b(x)} \quad (2) \log_e(10) = \frac{\log_e(x)}{\log_{10}(x)} \quad (3) 2.3026 = \frac{\ln(x)}{\log(x)}$$

Change of log base

$$\text{pH} \approx -\log_{10} \left[\frac{c(\text{H}^+)}{\text{mol L}^{-1}} \right] \quad \text{pOH} \approx -\log_{10} \left[\frac{c(\text{OH}^-)}{\text{mol L}^{-1}} \right]$$

Definitions: pH and pOH

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \text{Definition: autoprotolysis constant water}$$

$$\text{p}K_w = -\log_{10}(K_w) \quad \text{p}K_w = \text{pH} + \text{pOH} = 14 \quad \text{Definition: } \text{p}K_w$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Henderson-Hasselbalch equation

$$[\text{A}] = [\text{A}]_0 \exp(-kt)$$

First-order rate law

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$$

Log form of the Arrhenius equation

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Nernst equation for the Daniell cell

$$F = e N_A = 96485 \text{ C mol}^{-1}$$

Faraday constant

$$\Delta_r G^\circ = -RT \ln K_c^\circ$$

Standard Gibbs energy of reaction

$$n = n_0 \exp(-kt)$$

First-order radioactive decay

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

Photoelectric effect

$$\ln p \approx -\frac{\Delta_{\text{vap}} H}{RT} + C$$

Integrated Clausius-Clapeyron equation

$$f'(x_1) = \lim_{\Delta x \rightarrow 0} \frac{\Delta y}{\Delta x} = \frac{dy}{dx} \quad \text{Definition: differentiation of a function at } x_1$$

$$v = \frac{dd}{dt} \quad \text{Velocity is the differential of distance with time}$$

$$a = \frac{dv}{dt} = \frac{d}{dt} \left(\frac{dd}{dt} \right) = \frac{d^2d}{dt^2} \quad \text{Acceleration is the differential of the velocity with time}$$

$$F = m \times a \quad \text{Definition: force equals mass times acceleration}$$

$$f(c) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} c^2 \exp \left(-\frac{mc^2}{2k_B T} \right) \quad \text{Maxwell-Boltzmann speed distribution}$$

$$v = -\frac{d[A]}{dt} \quad \text{Definition: rate of reaction for a single reactant species A.}$$

$$\frac{d(uv)}{dx} = u \frac{dv}{dx} + v \frac{du}{dx} \quad \text{The product rule for differentiation}$$

$$\frac{dy}{dx} = \frac{dy}{dn} \times \frac{dn}{dx} \quad \text{Chain rule for differential of a function } y = f(n) \text{ where } n = f(x)$$

$$\frac{de^n}{dx} = \frac{dn}{dx} e^n \quad \text{The chain rule applied to } y = en \text{ where } n = f(x)$$

$$c_{mp} = \sqrt{\frac{2k_B T}{m}} \quad \text{Definition: most probable speed of gas molecule}$$

$$V = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{Lennard-Jones potential}$$

$$\text{pH} = -\log[\text{H}^+] \quad \text{Definition: pH of a solution}$$

$$\frac{d[A]}{dt} = -k[A] \quad \text{Rate of reaction for radioactive decay}$$

$$(1) \frac{d[A]}{dt} = -\overbrace{k[A]^2}^{\text{A} \rightarrow \text{P}} \quad (2) \frac{d[A]}{dt} = -\overbrace{k[A][B]}^{\text{A+B} \rightarrow \text{P}} \quad \text{Definition: second-order rate laws}$$

$$w = -\int_{V_i}^{V_f} p_{\text{ex}} dV \quad \text{Work done on the system by a reversible expansion}$$

$$\int \frac{1}{x} dx = \ln(x) + C \quad \text{Standard integral of a reciprocal of a variable}$$

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

$$\frac{[A]_t}{[A]_0} = \exp(-kt) \quad [A]_t = [A]_0 \exp(-kt) \quad \text{Integrated first-order rate law}$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k t \quad \text{Integrated second-order rate law with one reactant}$$

$$w = -nRT \ln \frac{V_f}{V_i} \quad p\text{-}V \text{ work done on the system in an ideal gas expansion}$$

$$\begin{aligned} \frac{C_p^\circ}{R} &= a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4 \\ \frac{H^\circ}{RT} &= -a_1 T^{-2} + a_2 \frac{\ln(T)}{T} + a_3 + a_4 \frac{T}{2} + a_5 \frac{T^2}{3} + a_6 \frac{T^3}{4} + a_7 \frac{T^4}{5} + \frac{b_1}{T} \\ \frac{S^\circ}{R} &= -a_1 \frac{T^{-2}}{2} - a_2 T^{-1} + a_3 \ln(T) + a_4 T + a_5 \frac{T^2}{2} + a_6 \frac{T^3}{3} + a_7 \frac{T^4}{4} + b_2 \end{aligned} \quad \text{NASA polynomial equations}$$

$$C_p^\circ = \left(\frac{\partial H^\circ}{\partial T} \right)_p \rightarrow \Delta H^\circ = \int_{T_1}^{T_2} C_p^\circ dT \quad \text{Constant pressure heat capacity and enthalpy}$$

$$\Delta S^\circ = \frac{\Delta H^\circ}{T} \rightarrow \Delta S^\circ = \int_{T_1}^{T_2} \frac{C_p^\circ}{T} dT \quad \text{Constant pressure heat capacity and entropy}$$

$$\int \sin^2(ax) dx = \frac{x}{2} - \frac{1}{4a} \sin(2ax) + C \quad \text{Standard integral for a sine squared function}$$

$$P(r) = \frac{4}{a_0^3} r^2 \exp\left(-\frac{2r}{a_0}\right) \quad \text{Radial distribution function for a 1s electron of a H-atom}$$

A	B	
du/dx	$\int v dx$	
x^2	$\exp(bx)$	
$2x$	$\frac{1}{b} \exp(bx)$	Integration by parts, tabular method
2	$\frac{1}{b^2} \exp(bx)$	
0	$\frac{1}{b^3} \exp(bx)$	

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{Wavefunctions for a particle in a one-dimensional box}$$