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Description	**A workbook containing essential mathematical techniques for chemistry students**
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Introduction

Much of chemistry is quantitative. In the laboratory you will need to calculate yields, do calculations involving *pH* and pK_a, plot graphs and estimate experimental errors. To follow the core chemistry lectures you will need a mastery of simple algebra, trigonometry and calculus. In short to get the most out of this course and to get good marks in examinations and practical work, you need a certain level of mathematical skills. This course aims to equip you with these skills.

There are several important points to note about this course.

Chem 10511 is student centred learning. This means you have the full course material, practice exercises and answers to the exercises plus video screencasts of worked solutions for some of the exercises. *You work through this material at your own pace in your own time*. In addition a practice exam test is provided for each of the real tests - so that you know the sort of thing to expect in the real test. All up to date information on the course should be accessed through the Chem 10511 Blackboard site.

- You work though the material in your own time at your own pace, using the workbook, screencasts and on-line practice tests.
- There is a drop-in clinic every Friday in Room 7.29 between 1.0 – 2.0 pm
- Specialised PASS sessions are conducted to provide assistance.
- Assessment is *via* three Blackboard Tests.

The drop-in clinic (in my office 7.29) is to go through particular problems that you still don't understand - even with the course material, screencasts and answers. *Bring along you working/attempts* so we can go through the problem together. This is a clinic – it does not contain lectures or formal presentations.

The material covered is divided into 3 sections each of which are examined using a Blackboard test. The 3 sections are presented in the workbook under headings Tests 1, 2 and 3. You will be divided into 3 or 4 groups for each test. You will be given 45 minutes to complete each test. Please consult the Blackboard site for all up to date information concerning group allocations near to the test dates. All tests will take place in the Chemistry Computer Cluster on the ground floor of the Chemistry building.

All tests take place between 1-5 pm on the following dates:

Test 1	23rd October 2009.
Test 2	13th November 2009.
Test 3	11th December 2009.

For the overall mark the individual tests are weighted in the ratio 20:30:50 for tests 1, 2 and 3 respectively.

These tests will be invigilated and University regulations will apply. Library cards must be on view. No notes or text-books may be used.

- Practice Blackboard test quizzes are available for use at any time. We strongly recommend that you try these before attempting the real test. To access these follow the links on the Blackboard site.

- Bring paper and pens with you to these tests. For the first test no calculators are allowed, but these will be needed for tests 2 and 3.

- A useful textbook to accompany the course is:

  Beginning Mathematics for Chemistry, S K Scott, OUP (1995)

- A final word – we believe it extremely important that all our students have a mastery of the mathematical skills contained in this course. Please note, however, that we are not asking for an impossibly high standard! Many of you will have covered much of the material already – for those of you who have not - on satisfactory completion of this course, you will have acquired these skills.

Test 1 Material

Algebra

A natural starting point in any mathematics education is algebra. The ability to perform basic algebraic manipulations, to expand or factorise expressions and rearrange formulae, is fundamental to handling of numerical data and developing physical models of the way the universe works.

> You should always bear in mind that algebra is nothing more than common sense! It is simply a way of stating systematically what we are allowed to do with **numbers**. Remember, at the end of the day, the letters in algebraic expressions simply stand for numbers and we are dealing with nothing more than **arithmetic**.

Our starting point is to define carefully the properties of numbers.

Negative Numbers

Before we look at some basic algebra it is important that you are clear on the use of negative numbers.

The early history of real numbers had three important stages.

Positive numbers 1, 2, 3 ....

These developed from the need to count objects - sheep, coins etc.

e.g. $3 + 2 = 5$ $\quad 7 - 6 = 1$

Zero

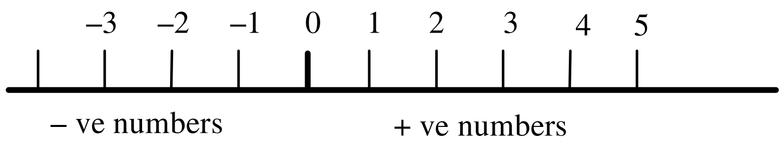
The inclusion of zero as a number is a later (Arabic) idea. It simplifies calculations. e.g. $3 - 3 = 0$

Negative numbers –1, –2, –3 …

The idea of negative numbers is later still. They greatly simplify the rules of algebra and are fundamental to everyday scientific expressions.

e.g. $5 - 8 = -3$

Real numbers



Adding a negative number is the same as subtracting a positive number.

$$a + -b = a - b$$

Subtracting a negative number is the same as adding a positive number.

$$a - -b = a + b$$

Multiplication rules

positive × positive = positive	$a \times b = ab$
positive × negative = negative	$a \times -b = -ab$
negative × positive = negative	$-a \times b = -ab$
negative × negative = positive	$-a \times -b = ab$

Arithmetic - basic rules

Addition

$a + b = b + a$ The order doesn't matter

e.g. $2 + 5 = 5 + 2$ Both equal 7

Multiplication

$a \times b = b \times a$ The order doesn't matter

e.g. $2 \times 5 = 5 \times 2$ Both equal 10

Subtraction

$a - b \neq b - a$ The order matters

$a - b = -(b - a)$

e.g. $2 - 5 \neq 5 - 2$ $-3 \neq 3$

Division

$\frac{a}{b} \neq \frac{b}{a}$ The order matters $\frac{a}{b} = \frac{1}{\frac{b}{a}}$

e.g. $\frac{2}{5} \neq \frac{5}{2}$ $0.4 \neq 2.5$

Common Factors - expanding

$a(x + y) = ax + ay$

$a(x - y) = ax - ay$

e.g. $2(3 + 4) = (2\times3) + (2\times4)$

$2(3 - 4) = (2\times3) - (2\times4)$

Multiplying Brackets

$(a + b)(c + d) = ac + ad + bc + bd$

$(x + a)(x + b) = x^2 + ax + bx + ab$

$= x^2 + (b + a)x + ab$

e.g. $(4 + 6)(2 + 5) = (4\times2) + (4\times5) + (6\times2) + (6\times5)$

Factorising

$$ac + ad + bc + bd = a(c + d) + b(c+d)$$
$$= (c + d)(a + b)$$
$$= (a + b)(c + d)$$

e.g. $(4\times 2) + (4\times 5) + (6\times 2) + (6\times 5) = 4(2 + 5) + 6(2 + 5)$
$$= (2 + 5)(4 + 6)$$
$$= (4 + 6)(2 + 5)$$

Factorising is just a useful way of tidying up expressions. In no way does it change the underlying value when numbers are substituted for the variables. Factorising expressions is somewhat of an art that only comes with plenty of practice.

Equations with a single variable

e.g. $y = 5x + 3$ $\quad y = \dfrac{10x}{(x+2)}$ $\quad y = ax^2 + bx + c$ $\quad y = \sin\left(\dfrac{x}{a}\right)$

You will meet many expressions of this type in the course. The equation has a single variable (x in these examples) and a number of constants (5, 3, a, b, c,...). It is **essential** that you can perform basic manipulation of these expressions.

More on multiplying brackets

$y = (5 + x)(x + 3)$	
$= (5\times x) + (5\times 3) + (x\times x) + (x\times 3)$	expand
$= 5x + 15 + x^2 + 3x$	simplify each term
$= x^2 + 5x + 3x + 15$	reorder
$= x^2 + (5 + 3)x + 15$	collect factors
$= x^2 + 8x + 15$	simplify factors

Both expressions are exactly the same in value. They are just different forms of the same thing.

General Rule

$(x + a)(x + b)$ $\quad = (x\times x) + (x\times b) + (a\times x) + (a\times b)$

$$= x^2 + bx + ax + ab$$

$= x^2 + (b+a)x + ab$

Special Cases

$(x + a)^2$	$= (x + a)(x + a)$	$= x^2 + 2ax + a^2$
$(x + a)(x - a)$	$= x^2 - ax + ax - a^2$	$= x^2 - a^2$
$(x - a)^2$	$= (x - a)(x - a)$	$= x^2 - 2ax + a^2$

Multiple brackets

$$(x + 1)(x + 2)(x + 3) = (x + 1)(x^2 + 5x + 6)$$

$$= x^3 + 5x^2 + 6x + x^2 + 5x + 6$$

$$= x^3 + 6x^2 + 11x + 6$$

Practice Exercise 1

Expand the following expressions

$(x + 1)(x + 6)$

$(4x + 1)(2x + 2)$

$(x + 4)(x - 6)$

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

$(2x - 1)(3x - 2)$

$(x - 1)(-x + 6)$

$(-x - 3)(-6x + 4)$

$(x + 1)^3$

$(x + a)^3$

Factorise the following expressions

$x^2 - 1$

$x^2 + 2x + 1$

$x^2 - 2x + 1$

Fractions

Addition and subtraction

$\frac{1}{2} + \frac{1}{3} = ?$ $\qquad \frac{3}{6} + \frac{2}{6} = \frac{5}{6}$ put over common denominator

WRONG $\qquad \frac{1}{a} + \frac{1}{b} \neq \frac{1}{a+b}$ $\qquad$ Common Error

$$\frac{1}{2} + \frac{1}{3} \neq \frac{1}{5}$$

The value of a fraction is not changed by multiplying top and bottom by the same number e.g.

$$\frac{1}{2} = \frac{2}{4} = \frac{3}{6}$$

This provides the method for adding and subtracting fractions

$$\frac{1}{a} + \frac{1}{b} = \frac{1 \times b}{a \times b} + \frac{1 \times a}{b \times a} = \frac{b+a}{ab}$$

$$\frac{1}{a} - \frac{1}{b} = \frac{1 \times b}{a \times b} - \frac{1 \times a}{b \times a} = \frac{b-a}{ab}$$

$$\frac{a}{x} + \frac{b}{y} = \frac{a \times y}{x \times y} + \frac{b \times x}{y \times x} = \frac{ay+bx}{xy}$$

Example

$$\frac{1}{5} + \frac{2}{x} = \frac{x + (5 \times 2)}{5x} = \frac{x+10}{5x}$$

going backwards

$$\frac{x+10}{5x} = \frac{x}{5x} + \frac{10}{5x} = \frac{1}{5} + \frac{2}{x}$$

Multiplication

$$\frac{1}{a} \times \frac{1}{b} = \frac{1}{ab}$$

$$\frac{a}{x} \times \frac{b}{y} = \frac{ab}{xy}$$

e.g. $\frac{8}{2} \times \frac{6}{3} = \frac{8 \times 6}{2 \times 3}$

Division

In ordinary arithmetic we can perform division by multiplying the nominator by the inverse of the denominator.

$a \div 3$	$=$	$a \times \frac{1}{3}$
division by 3		multiplication by 1/3

We do the same thing with fractions

$$\frac{1}{a} \div \frac{1}{b} = \frac{1}{a} \times \frac{b}{1} = \frac{b}{a}$$

$$\frac{\frac{a}{x}}{\frac{b}{y}} = \frac{a}{x} \div \frac{b}{y} = \frac{a}{x} \times \frac{y}{b} = \frac{ay}{bx}$$

Cancelling common factors

You can only cancel common factors in the numerator and denominator if they **multiply** everything else in both.

$$\frac{ax}{ay} = \frac{a}{a} \times \frac{x}{y} = \frac{x}{y} \qquad \frac{4(x+1)}{(x+2)(x+1)} = \frac{4}{(x+2)} \times \frac{(x+1)}{(x+1)} = \frac{4}{(x+2)}$$

$\frac{ax}{a+y}$ cannot cancel **a** since added in denominator

$\frac{4 + (x+1)}{(x+2)(x+1)}$ cannot cancel **(x+1)** since added in numerator

Practice Exercise 2

Evaluate the following expressions

$$\frac{1}{3} + \frac{1}{5}$$

$$\frac{2}{5} - \frac{4}{9}$$

$$\frac{2}{3} \times \frac{4}{9}$$

$$\frac{2}{3} \div \frac{4}{9}$$

$$\frac{2}{3x} + \frac{3}{y}$$

$$\frac{2}{3x} + \frac{3}{x}$$

$$\frac{1}{(x+2)} + \frac{1}{(x+3)}$$

$$(x+2) - \frac{6}{(x+3)}$$

Rearranging Equations

The basic form of an equation is Left hand Side (LHS) = Right Hand Side (RHS)

A key skill is to be able to perform manipulations on such equations. These are often done in order to isolate an expression for a particular variable. All valid manipulations do not alter the truth of the expression - they merely change the form.

There are really only **two rules** to manipulating equations:

An equation is unaffected if the same quantity is added or subtracted from each side

An equation is unaffected if each side is multiplied or divided by the same quantity

e.g. $x = y$

equally true are: $x + 3 = y + 3$ or $3x = 3y$ or $\frac{x}{a} = \frac{y}{a}$

These rules allow us to "move" constants, variable or expressions between sides.

$x + 7 = y$	initial equation
$x + 7 - 7 = y - 7$	subtract 7 from each side
$x = y - 7$	7 moved to other side

or

$9x = 5$	initial equation
$\frac{9x}{9} = \frac{5}{9}$	divide each side by 9
$x = \frac{5}{9}$	9 moved to other side

Isolating a variable

We can keep applying rules to isolate a variable on one side

$7x + 4 = 5$	initial equation
$7x + 4 - 4 = 5 - 4$	subtract 4 from both sides
$7x = 1$	moved the 4
$\frac{7x}{7} = \frac{1}{7}$	divide each side by 7
$x = \frac{1}{7}$	7 moved to other side

or

$\frac{7x + 4}{2 + y} = 10$	initial equation
$7x + 4 = 10(2 + y)$	multiply by (2 + y)
$7x = 10(2 + y) - 4$	subtract 4
$7x = 20 + 10y - 4$	expand
$7x = 16 + 10y$	
$7x = 2(8 + 5y)$	collect common factor
$x = \frac{2(8+5y)}{7} = \frac{2}{7}(8 + 5y)$	divide by 7

An examination of the above examples provides simpler rules for getting the same results.

<u>To move an expression following a + or – sign to the other side we simply change its sign</u>

$x - \mathbf{9} = 2y$	becomes	$x = 2y + \mathbf{9}$
$x + \frac{\mathbf{4y}}{\mathbf{3 + y}} = 5$	becomes	$x = 5 - \frac{\mathbf{4y}}{\mathbf{3 + y}}$

To move a nominator or denominator across we multiply by the inverse

$\mathbf{9}x = 2y$	becomes	$x = \frac{2y}{\mathbf{9}}$
$\mathbf{4y}x = 5$	becomes	$x = \frac{5}{\mathbf{4y}}$
$\frac{x}{\mathbf{y+3}} = 2$	becomes	$x = 2\mathbf{(y+3)}$

Chemistry Related Example

The 2nd order kinetics expression for the concentration of a species with time t is given by:

$$\frac{1}{c} - \frac{1}{c_0} = kt$$

where c is the concentration at time t, c_0 is the initial concentration (at time zero) and k is the rate constant. Find an expression for c.

$\frac{1}{c} = kt + \frac{1}{c_0}$	move c_0 over
$\frac{1}{c} = \frac{c_0kt + 1}{c_0}$	put over common factor
$\frac{c_0}{c} = (1 + c_0kt)$	move bottom c_0 over
$c_0 = (1 + c_0kt)c$	move c over
$\frac{c_o}{(1 + c_0kt)} = c$	move $(1 + c_0kt)$ over – divide
$c = \frac{c_o}{(1 + c_okt)}$	swap LHS and RHS

Applying operations to both sides

This idea that providing we do the same thing to both sides we can't change the truth of the equation means that we can apply operations to both sides

e.g.	$x = y$	Initial equation
	$x^2 = y^2$	square both sides
	$\sqrt{x} = \sqrt{y}$	square root both sides
	$\frac{1}{x} = \frac{1}{y}$	invert both sides
	$\log(x) = \log(y)$	logarithms of both sides
	$\sin(x) = \sin(y)$	sine of both sides....

Examples

$\sqrt{(x+a)} = \frac{y}{y+b}$	initial eqn
$(x+a) = \left(\frac{y}{y+b}\right)^2$	square both sides
$(x+a) = \frac{y^2}{(y+b)^2}$	simplify
$x = \frac{y^2}{(y+b)^2} - a$	move **a** over

or

$(x+2)^2 = 9$	initial eqn
$\sqrt{(x+2)^2} = \sqrt{9}$	square root both sides
$x + 2 = 3$	evaluate
$x = 1$	move 2 over

BEWARE

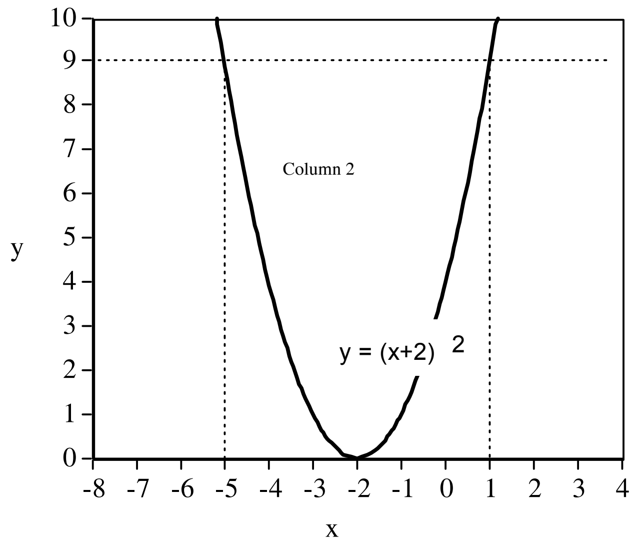
Some operations may not give a single answer. For instance the equation

$$(x + 2)^2 = 9$$

can be solved by taking the square root of each side but $\sqrt{9} = \pm 3$ so

$x + 2 = \pm 3$ is the full solution

$x = 1$ and $x = -5$ both answers are true.



In the graph, we have plotted the curve $y = (x+2)^2$. We have also drawn a horizontal, dotted line at $y = 9$. The two solutions to $(x+2)^2 = 9$ correspond to where the horizontal line intersects the solid – line curve. The vertical dotted lines are at $x = -5$ and $x = +1$, corresponding to the two solutions.

Sometimes we can rule out one of the solutions on physical grounds e.g.

$A = \pi r^2$ area of a circle

$r = \sqrt{\dfrac{A}{\pi}}$ only the positive root makes sense here.

Practice Exercise 3

Rearrange the following expressions to obtain x

$$x + 1 = 3$$

$$-4x + 1 = 2$$

$$\frac{(x + 4)}{3} = 2$$

$$(7x - 1) = 2(2x + 1)$$

$$\frac{(2x + 1)}{(3x - 2)} = 1$$

$$(x - 1)(x + 6) = x^2$$

$$\frac{(2x - a)}{(y + b)} = 4$$

$$\frac{(2x - a)}{y} = \frac{x}{3} + \frac{3}{y}$$

Practice Exercise 4

Rearrange the following expressions to obtain x

$$(x + 1)^2 = 16$$

$$\sqrt{\frac{x}{y}} = a + b$$

$$\sqrt{-4x+1} = y$$

$$\frac{1}{2}\ mx^2 = \frac{3}{2}\ kT$$

$$\frac{1}{\sqrt{x}} = \frac{1}{a} + \frac{1}{b}$$

In thermodynamics the Gibbs energy change for a reaction is given by

$\Delta G = \Delta H - T\Delta S$ find an expression for ΔS

The Van der Waals equation for a gas has the form

$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$ find an expression for p

Proportions and Percentages

It is often useful to give quantities as percentages.

To calculate the percentage, P, that a is of b

$$P = \frac{a}{b} \times 100\%$$

If we want to find the quantity represented by a certain percentage we work in reverse

$$a = \frac{P}{100} \times b$$

Examples:

1. What percentage is 43 of 179?

$$\text{percentage} = \frac{43}{179} \times 100\% = 24\%$$

2. What is 15% of 47?

$$a = \frac{15}{100} \times 47 = 7.05$$

3. A voltage is measured at 8 V with an uncertainty of ± 0.2 V. What is the percentage error?

$$\text{percentage error} = \pm\ \frac{0.2}{8} \times 100\% = \pm 2.5\%$$

4. A reaction produces a compound at a rate of 8 g min^{-1}. A catalyst raises this rate to 14 g min^{-1}. What is the percentage increase?

We can approach this in two ways

$$\text{percentage} = \frac{14}{8} \times 100\% = 175\%$$

i.e. 75% on top of the previous rate (since 8 g min^{-1} is 100%)

or

increase = 14 – 8 = 6 g min^{-1}.

$$\text{percentage} = \frac{6}{8} \times 100\% = 75\%$$

5. We perform an experiment to measure Planck's constant. We obtain 6.30 x 10^{-34} J s. The accepted value is 6.626 x 10^{-34} J s. What is the percentage error in our experiment?

$$\%\ \text{error} = \frac{\text{difference}}{\text{true value}} = \frac{6.30 \times 10^{-34} - 6.626 \times 10^{-34}}{6.626 \times 10^{-34}} \times 100\% = -4.9\%$$

Percentage Yield

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{maximum yield}} \times 100\ \%$$

1.6 g of methanol is mixed with excess ethanoic acid. After extraction the yield is 2.5 g of ester. What is the percentage yield?

$$CH_3OH + CH_3COOH \longrightarrow CH_3COOCH_3 + H_2O$$

Mol Wt CH_3OH = 32
Mol Wt CH_3COOCH_3 = 74

Stoichiometrically

32 g of CH_3OH yields 74 g of CH_3COOCH_3

1 g of CH_3OH yields $\frac{74}{32}$ g of CH_3COOCH_3

1.6 g of CH_3OH yields $\frac{74}{32} \times 1.6$ g = 3.7 g of CH_3COOCH_3

$$\text{percentage yield} = \frac{2.5}{3.7} \times 100\ \% = 67.6\ \%$$

Practice Exercise 5

What percentage is the first quantity of the second in the following?

(a) 27 of 54 **(b)** 0.15 of 0.37 **(c)** 61 of 48 **(d)** 17x of 51x

What value is represented by the following percentages?

(a) 23% of 41 **(b)** 150% of 0.3 **(c)** 2% of 10^{-21}

(d) 25% of (4x + 12)

A distance is measured as 10.3 ±0.2 miles. What is the percentage error?

A distance is measured as 5 miles ± 7%. What is the uncertainty in yards (1mile = 1760 yards)?

A fuel additive increases the engine performance from 36 mpg to 45 mpg. What is the percentage improvement?

Analysis and Presentation of Scientific Data

Much of chemistry is quantitative. In the laboratory you will need to manipulate data, present it in tabular and graphical form and analyse it to get useful results. Examinations and tutorial sheets also require you to be able to deal properly with numerical data. This section aims to familiarise you with such things as units, graph plotting and the analysis of experimental errors. As a word of encouragement, a tremendous number of marks are lost by students making mistakes in this area. A mastery of these topics can make the difference between a pass and a fail!

Powers of Ten

- Crop up frequently in science
- Important to manipulate them properly

Positive exponents

$10^1 = 10$

$10^2 = 10\times10 = 100$

$10^3 = 10\times10\times10 = 1000$

In general

$$\mathbf{10^n = \underbrace{10\times10\times\ldots}_{\text{n factors of 10}}\times10 = 100\ldots000 \ \ (n\ zeros)}$$

Negative exponents

$10^{-n} = 1/10^n$

i.e. $10^{-1} = \dfrac{1}{10} = 0.1$

$10^{-2} = \dfrac{1}{10^2} = 0.01$

$10^{-3} = \dfrac{1}{10^3} = 0.001$

In general

$$10^{-n} = \frac{\mathbf{1}}{\mathbf{10^n}} = 0.00\ldots0001 \text{ ([n–1] zeros)}$$

Note: $10^0 = 1$

Calculator warning!!

To get 10^3 enter 1Exp3 –

NOT 10Exp3 =10,000 = 10^4!

Scientific notation

Avoid writing very large or very small numbers out in full.

e.g. $123456 = 1.23456\times10^5$

$0.00023 = 2.3\times10^{-4}$

Test 1: 44444 =

0.00005 =

Manipulating powers of ten

Multiplication: $10^n\times10^m = 10^{n+m}$

i.e. $10^2\times10^3 = 10^{2+3} = 10^5$

$10^{-2}\times10^{-3} = 10^{-2-3} = 10^{-5}$

Test 2: $10^4\times10^{-2} =$

Division: $10^n/10^m = 10^{n-m}$

i.e. $10^3/10^5 = 10^{3-5} = 10^{-2}$

$10^2/10^{-4} = 10^{2-(-4)} = 10^{2+4} = 10^6$

Test 3: $10^{-2}/10^{-1} =$

Powers:

$(10^n)^m = 10^{n\times m}$

i.e. $(10^2)^3 = 10^2 \times 10^2 \times 10^2 = 10^{2\times 3} = 10^6$

The general rule works also with negative values of the exponents m and n, so

$$(10^{-2})^{-4} = 10^{(-2)\times(-4)} = 10^8$$

Test 4: $(10^{-2})^4 =$

Answers to Tests:
Test 1: 4.4444×10^4, 5×10^{-5}
Test 2: $10^{4-2} = 10^2$
Test 3: $10^{-2-(-1)} = 10^{-1}$
Test 4 $10^{(-2)\times 4} = 10^{-8}$

Dimensions and units

Most physical quantities are not just pure numbers. Typically they represent a quantity measured in certain units – e.g. a mass of 3 g, a temperature of 300 K.

In general

Physical quantity = number × unit

The seven independent basic physical quantities of the SI system, along with their symbols and units, are given below:

SI Base Quantities and Units

Quantity	Symbol	SI Unit	Unit Symbol
length	ℓ	metre	m
mass	m	kilogramme	kg
time	t	second	s
electric current	I	ampere	A
thermodynamic temperature	T	kelvin	K
amount of substance	n	mole	mol
luminous intensity	I_v	candela	cd

All other units can be constructed out of these.

e.g. speed = distance/time

Dimensions of speed = $\ell/t = \ell\, t^{-1}$

The dimension tells us how the quantity depends on the seven independent physical quantities listed above. Knowing the dimension, we can work out the unit.

Units of speed = m s^{-1}

Velocity – same dimensions and units as speed.

Acceleration = change of velocity/time

Dimensions $= \ell\, t^{-1}/\mathrm{t} = \ell\, t^{-2}$

Units = m s^{-2}

Force = mass × acceleration

Dimensions = $m \times \ell\, t^{-2} = m\, \ell\, t^{-2}$

Units = kg m s^{-2}

There are many units with special names derived from the basic list of seven given above; some of those most frequently used in chemistry are:

SI Derived Units with Special Names

Quantity	Name of unit	Symbol	Definition
frequency	hertz	Hz	s^{-1}
energy	joule	J	kg m^2 s^{-2}
force	newton	N	kg m s^{-2}
power	watt	W	J s^{-1}
pressure	pascal	Pa	N m^{-2}
electric charge	coulomb	C	A s
electric potential	volt	V	J A^{-1} s^{-1}
electrical resistance	ohm	Ω	V A^{-1}
electrical capacitance	farad	F	C V^{-1}
electrical conductance	siemens	S	A V^{-1}
magnetic flux density	tesla	T	kg s^{-2} A^{-1}

Clearly the definitions given above imply a whole series of relationships amongst these derived units; thus a joule is a newton metre, a watt second or a volt coulomb.

Some other quantities which are commonly used but which do not have named SI units are:

Quantity	Name of Unit	**Symbol**
volume	cubic metre	m^3
density	kg per cubic meter	$kg\ m^{-3}$
surface tension	newton per metre	$N\ m^{-1}$
dipole moment	coulomb metre	C m
magnetic moment	ampere square metre	$A\ m^2$
molar energy	U, H, A, G	$J\ mol^{-1}$
molar heat capacity	C_v, C_p	$J\ K^{-1}\ mol^{-1}$

Sometimes it is convenient to measure a quantity using SI units multiplied by powers of 10. Thus a distance could be 3 cm, a weight, µg, etc.

The permitted multiples in the SI are:

Fraction	Prefix	Symbol	Multiple	**Prefix**	Symbol
10^{-1}	deci	d	10	deka	da
10^{-2}	centi	c	10^2	hecto	h
$\mathbf{10^{-3}}$	**milli**	**m**	$\mathbf{10^3}$	**kilo**	**k**
$\mathbf{10^{-6}}$	**micro**	**µ**	$\mathbf{10^6}$	**mega**	**M**
$\mathbf{10^{-9}}$	**nano**	**n**	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E

Of these, deci- and centi- are used only occasionally, and deka- and hecto- hardly at all in this country. The commonly used multiples are shown in bold.

Thus 1 pN = 10^{-12} N; 1 MHz =10^6 Hz.

WARNING: NEVER FORGET TO PUT IN THE UNITS!!

Practice Exercise 6

1. Express the following numbers in scientific notation (e.g. 3123 becomes 3.123×10^{3})

   (i) 52,200

   (ii) 0.00025

2. Evaluate the following, leaving the answer in terms of powers of 10.

   (i) $(2\times10^{-5})\times(3\times10^{2})$,

   (ii) $\dfrac{4\times10^{-3}}{2\times10^{-5}}$,

   (iii) $\left(10^{-3}\right)^{-4}$

3. (i) Kinetic energy $=\dfrac{1}{2}mv^{2}$, where m is a particle's mass and v its speed.

   What are the dimensions of kinetic energy (i.e. in terms of ℓ, m, t, etc) and its units in terms of kg, m (metres) and s (seconds)?

   (ii) Pressure= force/area.

   What are the dimensions of pressure (i.e. in terms of ℓ, m, t, etc) and its units in terms of kg, m (metres) and s (seconds)?

Units from equations

We can predict units from an equation – often a useful trick! For example,

$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$, where

$\Delta_r H^0$ has units kJ mol^{-1} and T has units K. What are the units of $\Delta_r G^0$ and $\Delta_r S^0$?

To be consistent, $\Delta_r H^0$, $\Delta_r G^0$ and $T\Delta_r S^0$ must have the same units. Thus

Units of $\Delta_r G^0$: kJ mol^{-1}

Units of $T\Delta_r S^0$: kJ mol^{-1}

Thus units of $\Delta_r S^0$ are kJ K^{-1} mol^{-1}

Conversion of units

Sometimes you will need to convert units

e.g. kJ→J kg m^{-3} → g cm^{-3}

General rule

$$\boxed{\text{x old units} = \text{x} \times \frac{(\text{old units})}{(\text{new units})} \text{ new units}}$$

Examples

(i) 2 cm = ? m

$$2 \text{ cm} = 2 \times \left(\frac{\text{cm}}{\text{m}}\right) \text{m} = 2 \times \left(\frac{10^{-2}\text{ m}}{\text{m}}\right) \text{m} = 2 \times 10^{-2} \text{ m}$$

Check:

1 cm is shorter than 1 m. There are *fewer* metres in a given length than centimetres.

(ii) 2 mm^2 = ? cm^2

$$2\ \text{mm}^2 = 2\times\left(\frac{\text{mm}^2}{\text{cm}^2}\right)\text{cm}^2 = 2\times\left(\frac{\text{mm}}{\text{cm}}\right)^2\ \text{cm}^2 = 2\times\left(\frac{10^{-3}\ \text{m}}{10^{-2}\ \text{m}}\right)^2\ \text{cm}^2 = 2\times\left(10^{-1}\right)^2\ \text{cm}^2$$

$$= 2\times10^{-2}\ \text{cm}^2$$

Check:

1 cm^2 is a bigger area than 1 mm^2. Therefore fewer cm^2 fit into a given area than do mm^2.

The working given above was spelled out very fully. Clearly one can make short-cuts – e.g. one could immediately write (mm/cm)=1/10. Similarly some of the other steps can be missed out with practice. Nevertheless the method given will work every time without fail and can be very useful in the harder examples that follow.

Test 5: 2 nm^3 = ? mm^3

(iv) 3 cm^{-1} = ? m^{-1} (easy to get this wrong!!)

$$3\ \text{cm}^{-1} = 3\times\left(\frac{\text{cm}^{-1}}{\text{m}^{-1}}\right)\text{m}^{-1} = 3\times\left(\frac{\text{cm}}{\text{m}}\right)^{-1}\ \text{m}^{-1} = 3\times\left(\frac{10^{-2}\ \text{m}}{\text{m}}\right)^{-1}\ \text{m}^{-1} = 3\times\left(10^{-2}\right)^{-1}\ \text{m}^{-1} = 3\times10^{2}\ \text{m}^{-1}$$

Check:

More objects can fit into 1 m than into 1 cm. Thus the number in front of m^{-1} is bigger than that in front of cm^{-1}.

(v) 5 ms^{-2} = ? ns^{-2}

$$5\ \text{ms}^{-2} = 5\times\left(\frac{\text{ms}^{-2}}{\text{ns}^{-2}}\right)\text{ns}^{-2} = 5\times\left(\frac{\text{ms}}{\text{nm}}\right)^{-2}\text{ns}^{-2} = 5\times\left(\frac{10^{-3}\,\text{s}}{10^{-9}\,\text{s}}\right)^{-2}\text{ns}^{-2} = 5\times\left(10^{6}\right)^{-2}\text{ns}^{-2} = 5\times10^{-12}\ \text{ns}^{-2}$$

Please note that ms means a millisecond, not a meter second! A meter second would be written m s – i.e. with a space between the letters.

Test 6: 4 mm^{-3} = ? cm^{-3}

(vi) 2 mm μs^{-2} = ? m s^{-2}

$$2\ \text{mm}\,\mu\text{s}^{-2} = 2\times\left(\frac{\text{mm}\,\mu\text{s}^{-2}}{\text{m}\,\text{s}^{-2}}\right)\text{m}\,\text{s}^{-2} = 2\times\left(\frac{\text{mm}}{\text{m}}\right)\times\left(\frac{\mu\text{s}^{-2}}{\text{s}^{-2}}\right)\text{m}\,\text{s}^{-2} = 2\times\left(\frac{\text{mm}}{\text{m}}\right)\times\left(\frac{\mu\text{s}}{\text{s}}\right)^{-2}\text{m}\,\text{s}^{-2}$$

$$= 2\times\left(\frac{10^{-3}\,\text{m}}{\text{m}}\right)\times\left(\frac{10^{-6}\,\text{s}}{\text{s}}\right)^{-2}\text{m}\,\text{s}^{-2} = 2\times10^{-3}\times10^{12}\ \text{m}\,\text{s}^{-2}$$

$$= 2\times10^{10}\ \text{m}\,\text{s}^{-2}$$

So this is all there is to converting units – essentially all you need to know is how to manipulate powers of 10. A huge number of marks are lost in practical work and in examinations from wrongly converting units so make sure you fully understand how to do this.

Test 7: 3 g cm^{-3} = ? kg m^{-3}

Answers to Tests:

Test 5:

$$2\ \text{nm}^3 = 2\times\left(\frac{\text{nm}^3}{\text{mm}^3}\right)\text{mm}^3 = 2\times\left(\frac{\text{nm}}{\text{mm}}\right)^3\text{mm}^3 = 2\times\left(\frac{10^{-9}\,\text{m}}{10^{-3}}\right)^3\text{mm}^3 = 2\times\left(10^{-6}\right)^3\text{mm}^3 = 2\times10^{-18}\ \text{mm}^3$$

Test 6:

$$4\ \text{mm}^{-3} = 4\times\left(\frac{\text{mm}^{-3}}{\text{cm}^{-3}}\right)\text{cm}^{-3} = 4\times\left(\frac{\text{nm}}{\text{cm}}\right)^{-3}\text{cm}^{-3} = 4\times\left(\frac{10^{-3}\,\text{m}}{10^{-2}}\right)^{-3}\text{cm}^{-3} = 4\times\left(10^{-1}\right)^{-3}\text{cm}^{-3} = 4\times10^{3}\ \text{cm}^{-3}$$

Test 7:

$$3\ \text{g cm}^{-3} = 3\times\left(\frac{\text{g cm}^{-3}}{\text{kg m}^{-3}}\right)\text{kg m}^{-3} = 3\times\left(\frac{\text{g}}{\text{kg}}\right)\times\left(\frac{\text{cm}^{-3}}{\text{m}^{-3}}\right)\text{kg m}^{-3} = 3\times\left(\frac{\text{g}}{10^{3}\,\text{g}}\right)\times\left(\frac{10^{-2}\,\text{m}}{\text{m}}\right)^{-3}\text{kg m}^{-3}$$

$$= 3\times10^{-3}\times\left(10^{-2}\right)\text{kg m}^{-3} = 3\times10^{-3}\times10^{6}\text{kg m}^{-3} = 3\times10^{3}\text{kg m}^{-3}$$

Practice Exercise 7

1. From the equation $\Delta E = hc\bar{\nu}$, work out the units of $\bar{\nu}$, given that ΔE is in J, h is in J s and c is in m s^{-1}.

2. (i) What is 8 pm^3 in m^3?

   (ii) What is 4 ms^2 in s^2?

   (iii) What is 4 μg in kg?

3. What is

   (i) 2.0 cm^{-1} in m^{-1}?

   (ii) 4.0 ms^{-2} in s^{-2} ?

   (iii) 3.0 mmol cm^{-3} in mol dm^{-3} ?

4. What is:

   (i) 3 cm μs^{-2} in m s^{-2} ?
   (ii) 2 mm^3 ns^{-1} in m^3 s^{-1} ?

Tables and Graphs

Alternative notation (Guggenheim)

Force, $F = 3.1 \times 10^{-5}$ N

Can instead write

$$F/\left(10^{-5}\ \mathrm{N}\right) = 3.1$$

i.e. divide through by powers of 10 **and** units

Tables

Tables are a convenient way of presenting data.

Columns/rows are optimally labelled using the Guggenheim notation, choosing the powers of 10 to make numbers in table of a reasonable size

e.g. for a particle moving in the x-direction, we can set up a table as shown below:.

Displacement d at time t.

$d/(10^{-3}$ m)	15	21	**25**	29
$t/(10^{-5}$ s)	5	6	**7**	8

Suppose you want to know a value of d or t from the table – for example the values corresponding to the bold numbers. To do this, we may write

$d/(10^{-3}$ m) = 25 (directly from the table). Therefore $d = 25 \times 10^{-3}$ m
(multiplying through by the units and the correct power of 10).

Similarly:

$t/(10^{-5}$ s) = 7; thus $t = 7 \times 10^{-5}$ s

Practice Exercise 8

1. Calculate:

   (i) ΔA from $\Delta A = \Delta U - T\Delta S$, where $\Delta U = 3.0$ kJ, $T = 100$ K and $\Delta S = 8.0$ J K^{-1}

   (ii) E from $E = hcB$, where $h = 6 \times 10^{-34}$ J s, $c = 3 \times 10^{8}$ m s^{-1} and $B = 5$ cm^{-1}.

2. Kinetic data:

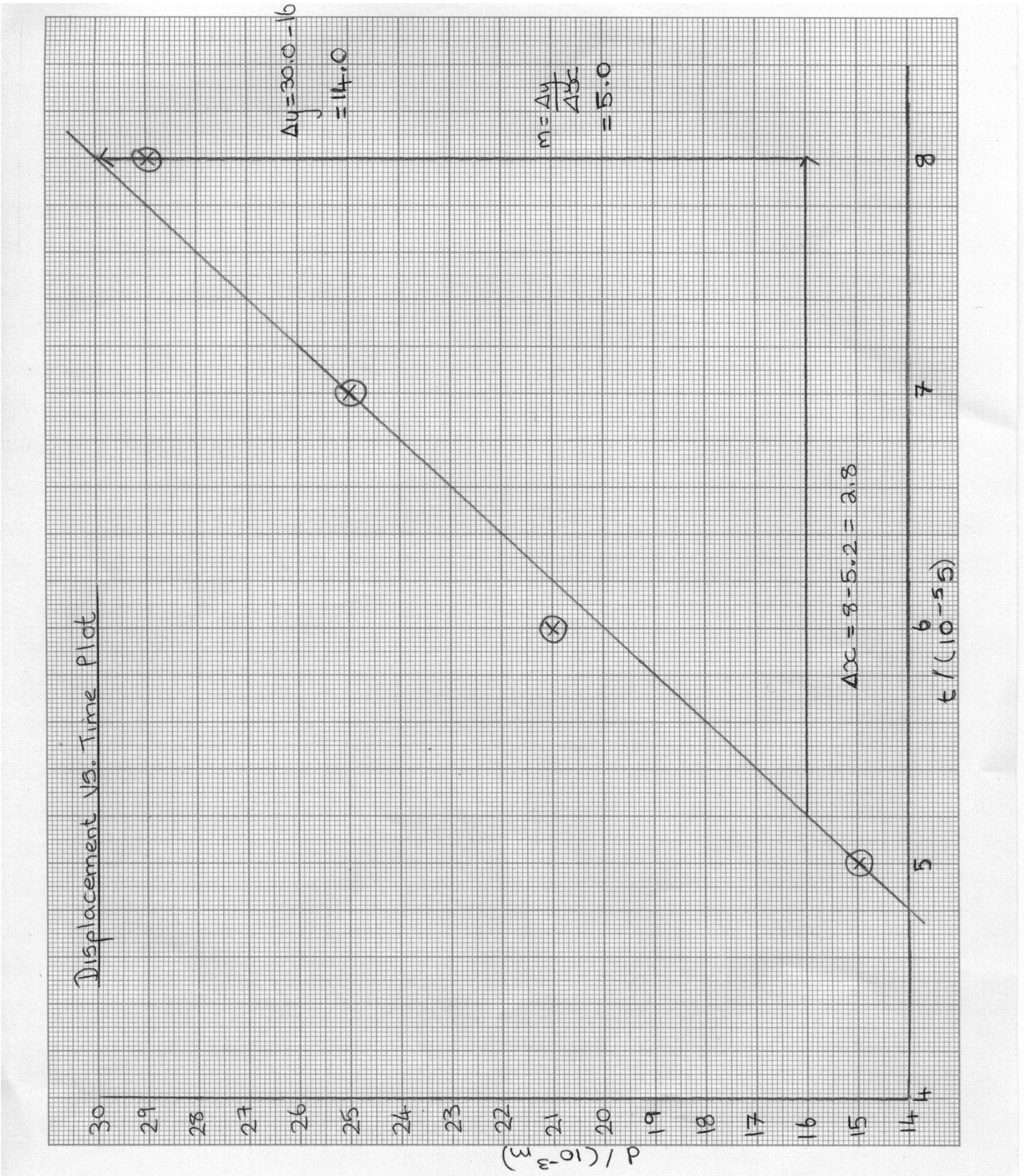
Time /(10^2 s)	0	1	**3**	7	13
Concentration /(10^{-3} mol dm^{-3})	10	8.5	**2.83**	1.72	0.96

   What time and what concentration correspond to the numbers in bold?

Graphs

Rules

1. Short, informative title
2. Label axes as in Table (i.e. to make numbers dimensionless and of reasonable size)
3. Choose scale to spread points out over the whole page. (*The origin need not be on the graph!*)
4. Draw a smooth curve (or straight line) through the points.



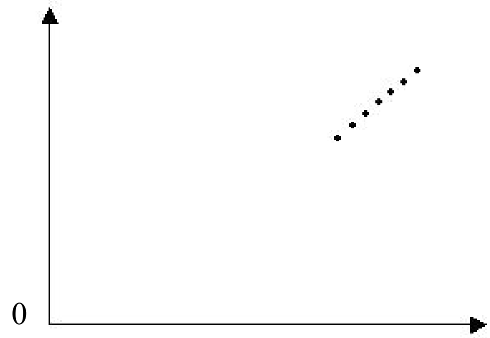
Example

Note: Origin not on graph.

Line – best attempt by eye to go near the points

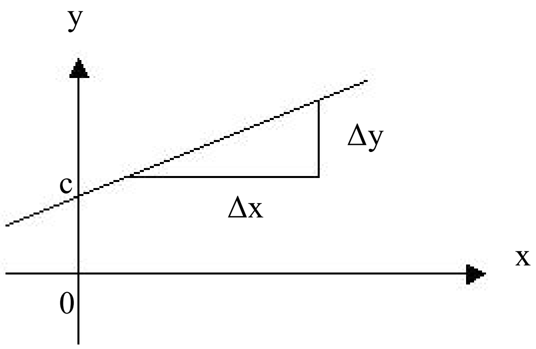
DO NOT DRAW THIS!!

(Leads to inaccuracies)



Straight Line Graphs

Many of the graphs you plot will be straight lines.



Equation of a straight line is:

$y = mx + c$ $\qquad\qquad$ m = gradient = $\Delta y/\Delta x$

Often m and c have physical significance and you need to calculate them.

Example

Our moving particle: $d = v\,t + d_0$

We did not plot d vs. t, we plotted $d/(10^{-3}$ m) vs. $t/(10^{-5}$ s) !

How do we find v?

Answer

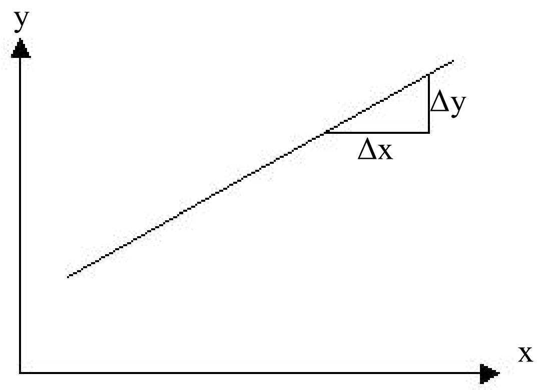
Let: $x = t/(10^{-5}\ \text{s})$; $y = d/(10^{-3}\ \text{m})$

i.e the axes of the graph as plotted.
Calculate gradient, *m*, of graph as plotted.

$$m = \frac{\Delta y}{\Delta x} = 5.0$$

Note: Choose Δx as big as possible to get an accurate value of *m*.

NOT:



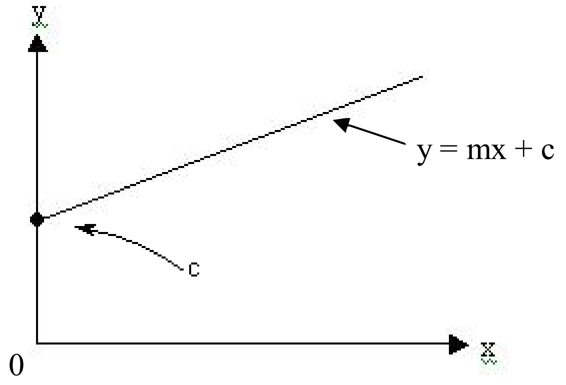
(GIVES INACCURATE ANSWERS)

Relation between *m* (dimensionless) and *v*?

$$\text{v} = \frac{\Delta \text{d}}{\Delta \text{t}} = \frac{\Delta \text{y} \times 10^{-3}\ \text{m}}{\Delta \text{x} \times 10^{-5}\ \text{s}} = \frac{\Delta \text{y}}{\Delta \text{x}} \times 10^{2}\ \text{m}\,\text{s}^{-1}$$
$$= 5 \times 10^{2}\ \text{m}\,\text{s}^{-1}$$

We regain correct units and correct power of 10.

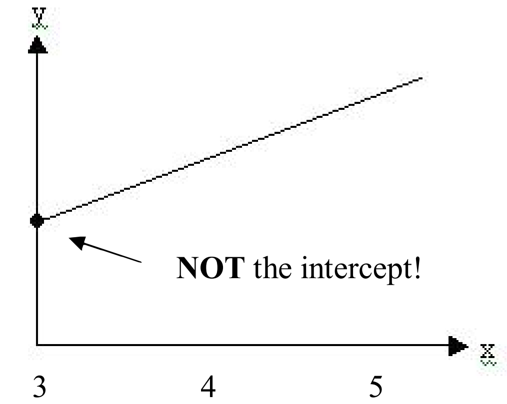
Calculating Intercepts



c = value of y when $x = 0$

Common Error

If you do not have the origin on your graph:



If the graph does not contain the origin, then you have to calculate c.

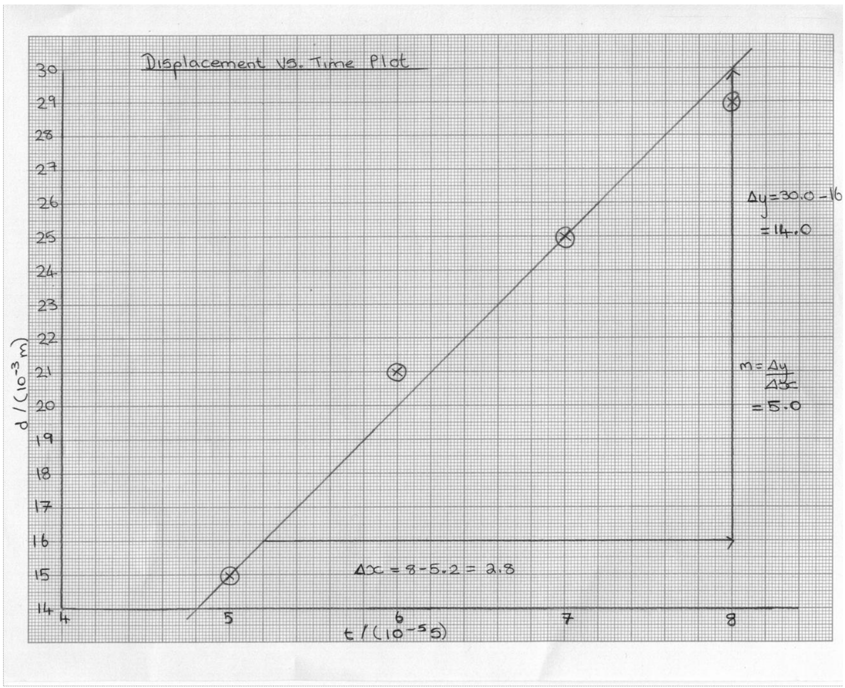
Procedure

1) Choose a value of x and read off the corresponding value of y (*on the line – not a data point*!)

2) $y = mx + c$; $\therefore c = y - mx$

   Given m and values for x and y, calculate c.

Example of moving particle



At $x = 6$, $y = 20$ (NB: *on* the line)

The slope $m = 5.0$ (from before)

So $\qquad c = y - mx$

$\qquad c = 20 - 5.0 \times 6 = -10$

We had: $\qquad d = v\,t + d_0$

We know c but what is d_0 ?

Recall: $x = t/(10^{-5}\text{ s})$; $\qquad y = d/(10^{-3}\text{ m})$

So: $\qquad c = d_0/(10^{-3}\text{ m})$

$d_0 = c \times 10^{-3}\text{ m} = -10 \times 10^{-3}\text{ m}$ – i.e. we regain units and powers of 10.

Practice Exercise 9

1. For one mole of ideal gas, $p = \left(\frac{R}{V_m}\right)T$, where p is the pressure, T is the absolute temperature, V_m is the molar volume and R is the gas constant.

   A chemist measures the dependence of p on T at a constant molar volume and obtains the following data:

Pressure / (10^6 Pa)	1.23	1.44	1.64	2.05	2.46
Temperature / (10^2 K)	3.00	3.50	4.00	5.00	6.00

   (i) Plot a graph of pressure against temperature:

   a) by hand

   b) using Excel (details of using Excel to plot graphs are given in the Communicating Chemistry module, Chem 10520).

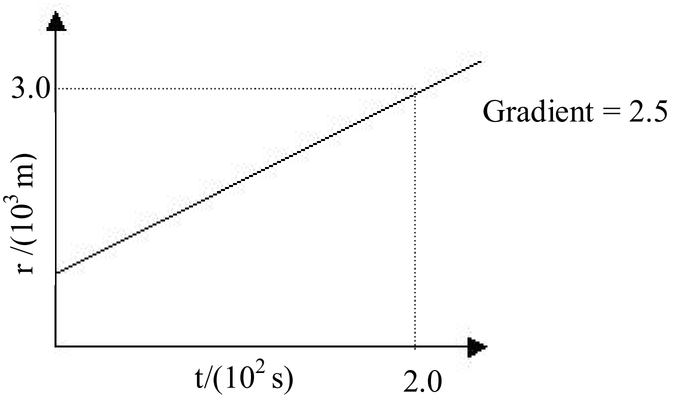
   (ii) Calculate the slope of the graph and thus estimate the value of $\left(\frac{R}{V_m}\right)$.

2. The position, r, of a particle moving with constant speed, v, was measured at various times, t. The equation of motion is

$$r = vt + r_0$$

   where r_0 is the initial position of the particle.

   A graph was plotted of r/(10^3 m) (y-axis) against t/(10^2 s) (x-axis), giving a straight line of gradient 2.5. At x = 2.0 the value of y was 3.0.



   Calculate the intercept of the graph and thence the value of r_0 in metres (m).

Test 2 Material

Significant Figures and Errors

Physical data is rarely totally accurate!

e.g. one measures a temperature, T, to a certain precision.

$T = 3.1 \times 10^3$ K

Means: T lies between 3.15×10^3 K and 3.05×10^3 K

More accurate measurement:

$T = 3.10 \times10^3$ K

Now: T lies between 3.105×10^3 K and 3.095×10^3 K

First case: 2 significant figures (sfs)

Second case: 3 significant figures (sfs)

Number of sfs are number of trustworthy figures.

Suppose: $F = m\ a$

$m = 1.0$ kg $\qquad$ $a = 3.0000$ m s^{-2} $\qquad$ $F = ?$

Rough rule

Quote answer to the least number of sfs in input data.

e.g $\qquad$ $F = 3.0$ N $\qquad$ (not: 3.0000 N)

Example

Calculate v from $v = \dfrac{\Delta x}{\Delta t}$

where $\Delta x = 2.0$ m and $\Delta t = 3.0$ s

Both Δx and Δy are given to 2 significant figures, so we quote v to 2 significant figures as well.

Thus $v = 0.67$ m s^{-1} (NOT 0.666666666666 m s^{-1} !)

Quote answer to a sensible number of significant figures!

Experimental Errors

Two main kinds:

(1) *Systematic*

e.g. faulty equipment or faulty calibration.
Reading *always* too high or too low.

(attempt to correct by calibration against known results)

(2) *Random*

e.g. deciding exactly when the end point of a titration is reached; accuracy of reading a dial .

Leads to a scatter of results about the true answer
(if no systematic error)

If only *one* measurement made:

estimate error as best one can

e.g. titre = 24.20 ± 0.02 cm^3

If *several* measurements made, proceed as follows.

Titration example:

titre/cm^3:	24.5	24.5	26.0

1) Calculate the *average*

$$\text{Average titre/cm}^3 = \frac{24.5 + 24.5 + 26.0}{3} = 25.0$$

This gives best estimate of the true value.

In general, for N data values (x_1, x_2, …x_N), we have

$$\bar{x} = \frac{x_1 + x_2 + \ldots + x_N}{N} = \frac{\sum_{i=1}^{N} x_i}{N}$$

2) Calculate the standard error of the mean, σ_m

$$\sigma_m = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \ldots + (x_N - \bar{x})^2}{N(N-1)}} = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N(N-1)}}$$

This measures the degree of scatter of data points about the mean.

In the example:

$$\sigma_m = \sqrt{\frac{(24.5 - 25.0)^2 + (24.5 - 25.0)^2 + (26.0 - 25.0)^2}{3 \times (3-1)}} = 0.5$$

Final answer is: titre/cm^3 = 25.0 ± 0.5

Interpretation

68% probability that true answer is in range $(\bar{x} - \sigma_m)$ to $(\bar{x} + \sigma_m)$

95% probability that true answer in range: $(\bar{x} - 2\sigma_m)$ to $(\bar{x} + 2\sigma_m)$

Note

Suppose $\bar{x} = 2.3692$ and $\sigma_m = 0.1234$

Answer is: 2.4 ± 0.1 (*possibly* 2.37 ± 0.12)

The error clearly indicates the number of significant figures.

Don't write all of the figures down!

Propagation of errors and linear regression

Suppose you need to combine experimental results (with errors) to get a final result.

How do you get the final error?

Rule 1

Z = cX, where c is an (exact) constant –no errors.

X has an error σ_X.

Error in Z, $\sigma_Z = c\sigma_X$ - i.e. you multiply the error by the constant.

e.g.

Z =3X; X = 2.0 ± 0.1

Z = 6.0 ± 0.3

Rule 2

Z = X + Y

or

Z = X – Y

Error on X is σ_X. Error on Y is σ_Y. Error on Z, σ_Z?

The rule for BOTH cases is:

$\sigma_Z^2 = \sigma_X^2 + \sigma_Y^2$, or $\sigma_Z = \sqrt{\left(\sigma_X^2 + \sigma_Y^2\right)}$

- i.e. you first square the errors, add the squares together, and then take the square root

e.g. X = 3.0 ± 0.3; Y = 2.0 ± 0.3

If Z = X – Y

Then: Z = 3.0 – 2.0 = 1.0

$$\sigma_Z^2 = (0.3)^2 + (0.3)^2 = 0.09 + 0.09 = 0.18$$
$$\sigma_Z = 0.42$$

Thus the final answer is: Z = 1.0 ± 0.4

A common mistake in this type of example is to subtract the errors. In this case this would give the very odd result that $\sigma_Z = 0$!

Rule 3

Suppose:

$Z = XY$

or

$Z = X/Y$

In both cases the rule is:

$$\left(\frac{\sigma_Z}{Z}\right)^2 = \left(\frac{\sigma_X}{X}\right)^2 + \left(\frac{\sigma_Y}{Y}\right)^2$$

e.g

$X = 1.0 \pm 0.1$ $\quad$ $Y = 3.0 \pm 0.5;$ $\quad$ $Z = ?$

$Z = X/Y = 0.333$

$$\left(\frac{\sigma_Z}{Z}\right)^2 = \left(\frac{0.1}{1.0}\right)^2 + \left(\frac{0.5}{3.0}\right)^2 = 0.0377$$

$$\frac{\sigma_Z}{Z} = 0.19$$

$$\sigma_Z = 0.19 \times 0.333 = 0.064$$

$\therefore$ **Z = 0.33 ± 0.06**

Remember to write down the final result and the error estimate to a sensible number of significant figures.

The rules can be extended to deal with more complicated situations involving the propagation of errors, but the above cases are the most important ones. Do note that the rules can be used in combination,

e.g. $Z = 2X + 3A/B$

$X = 2.0 \pm 0.2$; $A = 4.0 \pm 0.2$; $B = 6.0 \pm 0.3$.

Error in $2X = 2 \times 0.2 = 0.4$ (Rule 1)

Error in $A/B = 0.047$ (Rule 3 – check!)

Error in $3A/B = 0.141$ (Rule 1)

Error in Z = 0.315 (Rule 2 – check!)

Thus: Z = 6.0 ± 0.3 (writing everything to a sensible number of significant figures)

Linear Regression

Often data points are scattered about the best straight line.

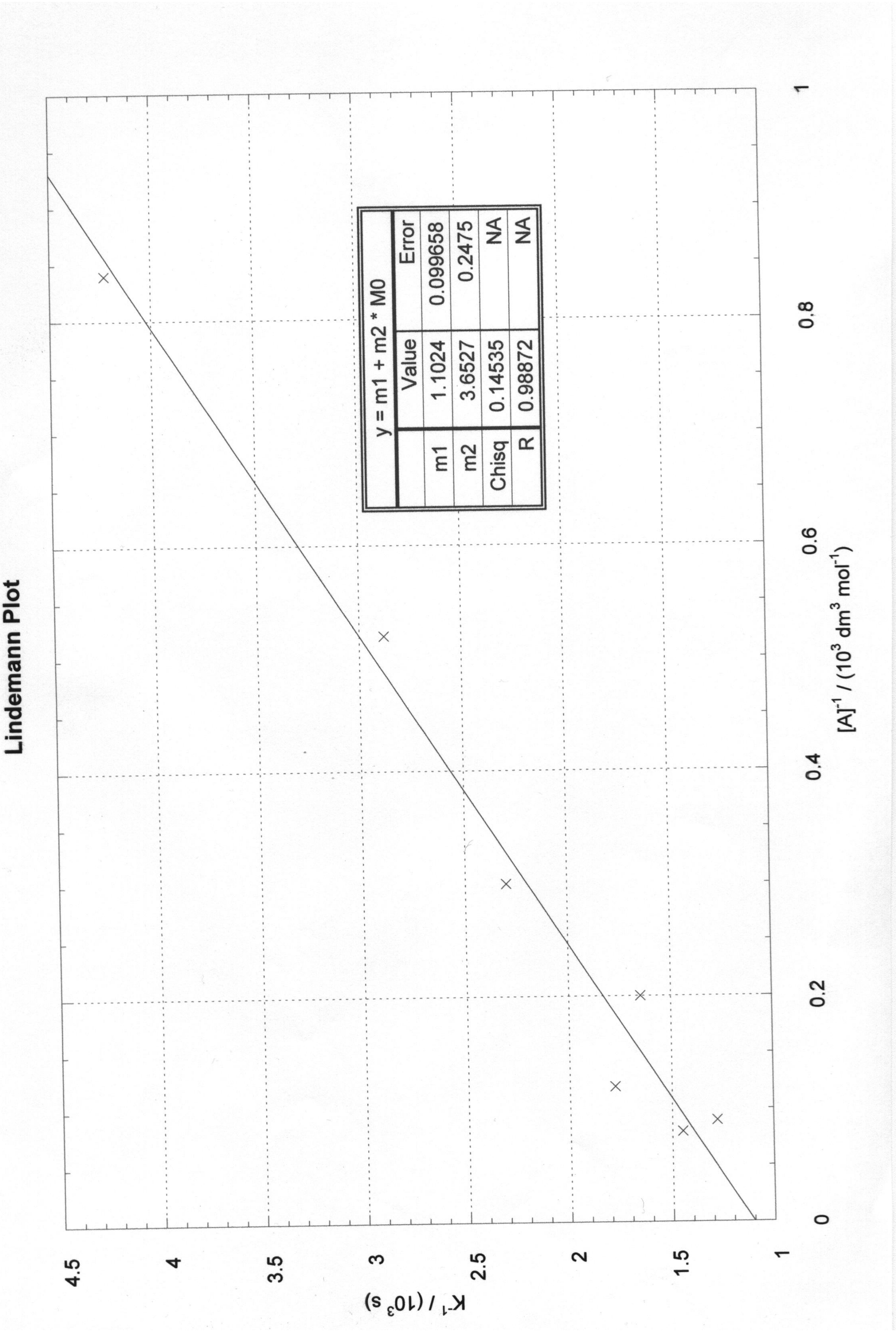
Linear regression or least squares fitting provides a way of determining the best straight line through the points and provides error estimates on the gradient and intercept.

In example (next page):

gradient (i.e. m_2) = 3.7 ± 0.2

intercept (i.e. m_1) = 1.10 ± 0.10

A computer program (Kaleidograph or Excel) will do this.


Lindemann Plot
y = m1 + m2 * M0
Value Error
m1 1.1024 0.099658
m2 3.6527 0.2475
Chisq 0.14535 NA
R 0.98872 NA
k^{-1} / (10^3 s)
$[A]^{-1}$ / (10^3 dm^3 mol^{-1})
4.5
4
3.5
3
2.5
2
1.5
1
0
0.2
0.4
0.6
0.8
1

Practice Exercise 10

1. Three measurements of an equilibrium constant, K (dimensionless!), were as follows;

   2.0, 7.0 and 3.0.

   Calculate the mean and the error, quoting the final result to a sensible number of significant figures.

2. Suppose $A = 4.0 \pm 0.4$ and $B = 3.0 \pm 0.3$. Calculate the value of C and its error in the following cases:

   (i) $C = A - B$

   (ii) $C = A + B$

   (iii) $C = 2A$

3. Suppose $A = 1.0 \pm 0.3$ and $B = 2.0 \pm 0.8$. Calculate the value of C and its error in the following cases:

   (i) $C = A \times B$

   (ii) $C = B/A$

Simultaneous equations

simplest form **Z = expression1**

and

Z = expression2

hence **expression1 = expression2**

This is an example of **substitution**. We use the first equation to get an expression for **Z** and substitute this expression in place of **Z** in equation 2.

This is also an example of simultaneous equations, where a variable is related to two equations which must both be true simultaneously.

e.g.

The Gibbs energy of a reaction, ΔG^0, is related to the enthalpy, ΔH^0, and the entropy, ΔS^0. The Equilibrium constant K is also related to the Gibbs energy. Thus

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

and

$$\Delta G^0 = -RT\ \ln(K)$$

Hence

$$-RT\ \ln(K) = \Delta H^0 - T\Delta S^0$$

$$\ln(K) = \frac{\Delta H^0 - T\Delta S^0}{-RT} = \frac{\Delta H^0}{-RT} - \frac{T\Delta S^0}{-RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

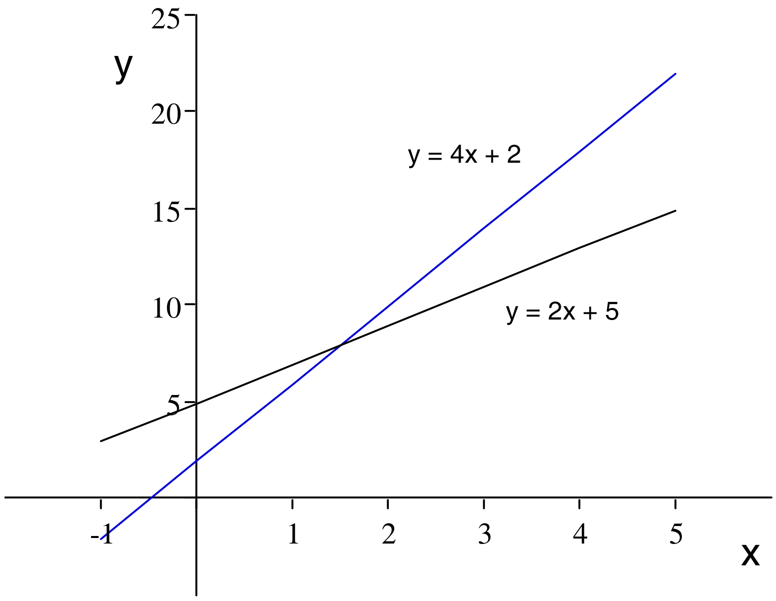
$$\mathbf{\ln(K) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}}$$

Simple simultaneous eqns in two variables

e.g. $y = 2x + 5$ and $y = 4x + 2$

these are just equations of straight lines and we can plot them simply.

x	**y = 2x + 5**	**y = 4x + 2**
–1	3	–2
0	5	2
1	7	6
2	9	10
3	11	14
4	13	18
5	15	22



We want to know the place at which they cross (i.e. where they have the same y value).

$4x + 2 = 2x + 5$

$4x – 2x = 5 – 2$

$2x = 3$ so $\underline{\mathbf{x = 1.5}}$

so $\mathbf{y} = 4 \times 1.5 + 2 = 6 + 2 = \mathbf{8}$ (equation 1)

or $\mathbf{y} = 2 \times 1.5 + 5 = 3 + 5 = \mathbf{8}$ (equation 2)

In general we have

$y = ax + b$ and $y = cx + d$

$ax + b = cx + d$

$ax - cx = d - b$

$x(a - c) = d - b$

$$\mathbf{x = \frac{d - b}{a - c}}$$

and putting this into either equation will yield the answer for y

$$y = a\left(\frac{d-b}{a-c}\right) + b \qquad\qquad y = c\left(\frac{d-b}{a-c}\right) + d$$

$$y = \frac{a(d-b) + b(a-c)}{a-c} \qquad\qquad y = \frac{c(d-b) + d(a-c)}{a-c}$$

$$y = \frac{ad - ab + ba - bc}{a-c} \qquad\qquad y = \frac{cd - cb + ad - cd}{a-c}$$

$$\mathbf{y = \frac{ad - bc}{a-c}} \qquad\qquad \mathbf{y = \frac{ad - bc}{a-c}}$$

We can test these out with the previous example, a = 4, b = 2, c = 2, d = 5

$$x = \left(\frac{d-b}{a-c}\right) = \left(\frac{5-2}{4-2}\right) = \frac{3}{2} = \mathbf{1.5}$$

$$y = \frac{ad - bc}{a-c} = \left(\frac{4 \times 5 - 2 \times 2}{4-2}\right) = \frac{16}{2} = \mathbf{8}$$

Further example

suppose we have $3y = 4x - 2$ and $2y = 6x + 2$ what do we do?

the trick is to get both expressions into the form above.

$y = \frac{4}{3}x - \frac{2}{3}$ divide first by 3

$y = 3x + 1$ divide second by 2

we can now use the formulae above to give us the solutions for **x** and **y**.
($x = -1$, $y = -2$)

Practice Exercise 11

Find the values of x and y in the following

$y = 3x + 1$

$y = 2x + 3$

$y = 3x - 1$

$y = 2x + 3$

$3y = 9x + 12$

$y = 2x - 3$

$3y = 3x - 15$

$2y = -4x - 6$

In thermodynamics the Equilibrium constant changes with temperature according to

$$\mathbf{RT\ ln(K) = -\Delta H^0 + T\Delta S^0} \qquad \mathbf{(R = 8.314\ J\ K^{-1}\ mol^{-1})}$$

write this in the form ΔH^0 = ...

then find ΔH^0 and ΔS^0 using the experimental values

ln(K) = 4 at T = 500 K and ln(K) = – 4 at T = 1000 K

Quadratic equations

These are equations of the form

$$ax^2 + bx + c = 0$$

There are two solutions to such an equation which are given by:

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

Matching a, b and c

a, b and c must be carefully matched in order to use the formula correctly, e.g.

$x^2 + x - 2 = [1]x^2 + [1]x + [-2]$ $\quad$ $a = 1, b = 1, c = -2$

$2x^2 - 3x + 8 = [2]x^2 + [-3]x + [8]$ $\quad$ $a = 2, b = -3, c = 8$

$-x^2 - x/2 + 1 = [-1]x^2 + \left[-\frac{1}{2}\right]x + [1]$ $\quad$ $a = -1, b = -1/2, c=1$

Not all quadratic equations have real solutions

If $\mathbf{b^2}$ is smaller than **4ac**, then $\mathbf{(b^2 - 4ac)}$ is negative and we cannot take the square root. (In fact such quadratic equations have imaginary roots, but we will not deal with that here).

Example

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

so $a = 1$, $b = 2$, and $c = -3$

$$x = \frac{2 \pm \sqrt{2^2 - 4 \times (1) \times (-3)}}{2} = \frac{-2 \pm \sqrt{4 + 12}}{2} = \frac{-2 \pm \sqrt{16}}{2} = \frac{-2 \pm 4}{2}$$

$$x = \frac{-2 + 4}{2} = 1 \quad \text{or} \quad x = \frac{-2 - 4}{2} = -3$$

we can use these answers to write the quadratic equation in a factorised form

$x = 1$ $\qquad$ $x = -3$

$x - 1 = 0$ $\qquad$ $x + 3 = 0$

hence

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

we can check this is the original eqn by multiplying out the brackets

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

Another Example

$$6x^2 - 7x + 2 = 0$$

so $a = 6$, $b = -7$, and $c = 2$

$$x = \frac{7 \pm \sqrt{(-7)^2 - 4 \times 6 \times 2}}{2 \times 6} = \frac{7 \pm \sqrt{49 - 48}}{12} = \frac{7 \pm 1}{12}$$

$$x = \frac{2}{3} \quad \text{or} \quad x = \frac{1}{2}$$

we can write the quadratic in factorised form from these

$$x = \frac{2}{3} \quad \text{so} \quad 3x = 2 \quad \text{or} \quad \underline{3x - 2 = 0}$$

$$x = \frac{1}{2} \quad \text{so} \quad 2x = 1 \quad \text{or} \quad \underline{2x - 1 = 0}$$

$$\underline{(3x - 2)(2x - 1) = 0}$$

Chemical example - dissociation equilibrium

	AB $\Longleftrightarrow$	**A** +	**B**
initial concs/(mol dm^{-3})	a_0	0	0
equilibrium concentration/(mol dm^{-3})	$a_0 - x$	x	x

where x is the amount that has reacted at equilibrium

$$K_{eq} = \frac{x \times x}{a_0 - x} = \frac{x^2}{a_0 - x}$$

we can solve this for x

$$\frac{x^2}{a_0 - x} = K_{eq}$$

$$x^2 = K_{eq}(a_0 - x)$$

$$x^2 - K_{eq}(a_0 - x) = 0$$

$$x^2 - K_{eq}a_0 + K_{eq}x = 0$$

$$x^2 + K_{eq}x - K_{eq}a_0 = 0$$

so we can solve this using a =1, b = K_{eq} and c = $-K_{eq}a_0$

$$x = \frac{-K_{eq} \pm \sqrt{K_{eq}{}^2 + 4K_{eq}a_0}}{2}$$

if a_0 = 0.1 and K_{eq} = 5 then

$$x = \frac{-5 \pm \sqrt{5^2 + 4 \times 5 \times 0.1}}{2} = \frac{-5 \pm \sqrt{27}}{2} = \frac{-5 \pm 5.196}{2}$$

since concentration must be positive the only real solution is

$$x = \frac{-5 + 5.196}{2} = \frac{0.196}{2} = \mathbf{0.098}$$

Therefore, equilibrium concentration of A is 0.098 mol dm^{-3}.

Practice Exercise 12

Solve the following quadratic expressions

$x^2 + x - 6 = 0$ $\quad\quad$ $a = 1, b = 1, c = -6$

$-2x^2 - x + 6 = 0$

$x^2 - \frac{x}{2} - \frac{1}{2} = 0$

$x + \frac{4}{x} = -5$

In overtone vibrational spectroscopy of HCl the energy of a transition, ΔE, is given by

$$\mathbf{\Delta E/cm^{-1} = 2991v - 53v(v+1)}$$

where **v** is a small integer (0–5). **v** is also known as the quantum number.

If a particular transition has an energy of 8347 cm^{-1} what is the quantum number **v**?

Powers and Exponents

Powers of 10

power	**prefix**	**symbol**		**power**	**prefix**	**symbol**
$10^1 = 10$	deca	da		$10^{-1} = 0.1$	deci	d
$10^2 = 100$	hecto	h		$10^{-2} = 0.01$	centi	c
$10^3 = 1000$	kilo	k		$10^{-3} = 0.001$	milli	m
10^6	mega	M		10^{-6}	micro	μ
10^9	giga	G		10^{-9}	nano	n
10^{12}	tera	T		10^{-12}	pico	p
				10^{-15}	femto	f

We express very large or very small numbers in terms of powers of 10 to avoid having to write long strings of zeros.

e.g. Mass of electron = 0.000000000000000000000000000000910908 kg
Charge of electron = 0.00000000000000000016021 C
Charge:mass ratio of electron = 175,879,600,000 C kg^{-1}

This is much better written as
Mass of electron = 9.10908×10^{-31} kg
Charge of electron = 1.66021×10^{-19}C
Charge:mass ration of electron = 1.758796×10^{11} C kg^{-1}

Combining powers of ten

$10^n \times 10^m = 10^{n+m}$ $100 \times 1000 = 100{,}000$ $10^2 \times 10^3 = 10^5$

$\dfrac{10^n}{10^m} = 10^{n-m}$ e.g $\dfrac{100}{1000} = 0.1$ $\dfrac{10^2}{10^3} = 10^{-1}$

This division rule is easy to understand since

$$10^{-m} = \frac{1}{10^m} \text{ hence } \frac{10^n}{10^m} = 10^n \times 10^{-m} = 10^{n-m}$$

Calculators - Beware!
Calculators usually use the letter E to stand for the power of ten. (E from **E**xponent)

10^n means 1 x 10^n so enter 1En NOT 10En (which is 10 x 10^n)

e.g. 1×10^3 is entered as 1E+3 1×10^{-3} is entered as 1E-3

Exponents

In 10^n the n is called the exponent. Exponents can be applied to any number.

$$10^3 = 10 \times 10 \times 10 \quad \text{and} \quad 5^4 = 5 \times 5 \times 5 \times 5$$

We can apply exponents to constants or variables

$$y^2 = y \times y \quad \text{or} \quad z^3 = z \times z \times z$$

the multiplication rule is easy to understand

$$10^2 \times 10^3 = (10 \times 10) \times (10 \times 10 \times 10) = 10^5$$

$$10^n \times 10^m = 10^{n+m} \text{ or generally } x^n \times x^m = x^{n+m}$$

Inverses

We define $x^{-1} = \frac{1}{x^1} = \frac{1}{x}$ or more generally $x^{-n} = \frac{1}{x^n}$

$$x^{-3} = \frac{1}{x \times x \times x} = \frac{1}{x^3} \quad \text{and} \quad (x-3)^{-2} = \frac{1}{(x-3)^2}$$

the division rule follows from this definition

$$\frac{10^2}{10^3} = 10^2 \times \frac{1}{10^3} = 10^2 \times 10^{-3} = 10^{2-3} = 10^{-1} = \frac{1}{10}$$

more generally $\frac{x^n}{x^m} = x^n \times \frac{1}{x^m} = x^n \times x^{-m} = x^{n-m}$

Special cases

Two exponent values need clarification

$x^1 = x$ anything raised to the power 1 is itself

$x^0 = 1$ anything raised to the power 0 is unity (1)

this last case is not immediately obvious but it makes sense if you consider

$10^{-3} = 0.0001$

$10^{-2} = 0.001$

$10^{-1} = 0.1$

$10^0 = 1$

$10^1 = 10$

$10^2 = 100$

$10^3 = 1000$

Roots

We can also express the roots of expressions as exponents. The simplest root is the square root.

$\sqrt{9} = 3 \quad \sqrt{16} = 4$

How do we write these as exponents? We want to write $\sqrt{x}$ in the form x^p

consider the expression

$y^2 = x \qquad (\text{so } y = \sqrt{x})$

clearly

$y \times y = x$

now $y = \sqrt{x} = x^p$ where p is the exponent that represents the square root

so $x^p \times x^p = x^1$

$x^{p+p} = x^1$

$x^{2p} = x^1$

this can only be true if $2p = 1$, so $p = \dfrac{1}{2}$ Hence we have $\sqrt{x} = x^{1/2}$

Equally the **n**th root is written as **1/n**

$$Z = y^3$$

then y is the cube root of z

$$y = \sqrt[3]{Z} = Z^{1/3}$$

most calculators have x^y and $\sqrt[x]{y}$ buttons to perform these functions.

We can handle roots easily using the usual rules

$$x^{1/2} \times x^{3/2} = x^{(1/2+3/2)} = x^2 \qquad \text{since } \frac{1}{2} + \frac{3}{2} = 2$$

Powers of Powers

$$(x^2)^2 = x^2 \times x^2 = x^4 \text{ and } (x^2)^3 = x^2 \times x^2 \times x^2 = x^6$$

$$(x^n)^m = x^{n \times m}$$

this can be used to split up complicated root expressions

$$x^{3/2} = (x^3)^{1/2} = \sqrt{x^3} \text{ since } 3 \times \frac{1}{2} = \frac{3}{2}$$

equally

$$x^{3/2} = (x^{1/2})^3 = (\sqrt{x})^3 \text{ since } \frac{1}{2} \times 3 = \frac{3}{2}$$

Practice Exercise 13

Express the following in their full form

(a) 2.998×10^8

(b) 3.4462×10^4

(c)123×10^5

(d) 1.7×10^{-5}

Express the following in powers of 10 (one figure before the decimal point)

(a) 101325

(b) 0.0000024

(c) 255×10^4

(d) 255×10^{-9}

What is the value of the following expressions ?

(a) $2^3 \times 2^4$

(b) $3^{-3} \times 3^{-1}$

(c) $\dfrac{\pi^3}{\pi^2 \times \pi}$

(b) $x^3 \times \dfrac{1}{x^2}$

(c) $4^{3/2}$

(d) $8^{-2/3}$

(g) $\dfrac{y^{1/2}}{y^{3/2}}$

(h) $\dfrac{x^{3/2}}{x^{0.75} \times x^{0.75}}$

Expand

(a) $(x^2)^5$

(b) $(x^2)^{5/2}$

(c) $\dfrac{\sqrt{\pi^3}}{\pi}$

(d) $x^{2/3} \times \dfrac{1}{\sqrt{x}}$

Simplify

(a) $(x^2 + 2x + 1)^{1/2}$ **(b)** $\dfrac{\sqrt{x^2 - 2x + 1}}{x^2 - 1}$

Exponential Function (e)

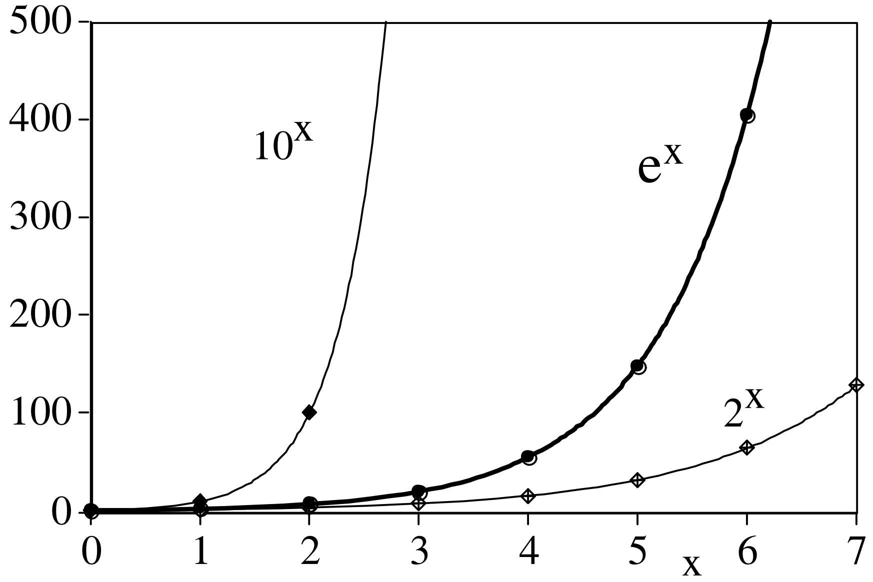
We have already dealt with the rules for handling exponents. The most common number which we use exponents with is 10 e.g. 2×10^3 or 3×10^{-4}. There is, however, another number which occurs throughout mathematics, physics and chemistry. It is given the symbol **e**. It is an 'irrational' number (like π) which cannot be represented exactly.

$e = e^1 = 2.7182818284...$ $\quad e^2 = e \times e = 7.3890560989$

Exponential Function - e^x is sometimes written as exp(x) or Exp(x)

Remember, **e** is just a number so $\mathbf{e^x}$ is not intrinsically different from 2^x or 10^x.

x	$\mathbf{2^x}$	$\mathbf{e^x}$	$\mathbf{10^x}$
0	1	1.00	1
1	2	2.72	10
2	4	7.39	100
3	8	20.09	1000
4	16	54.60	10000



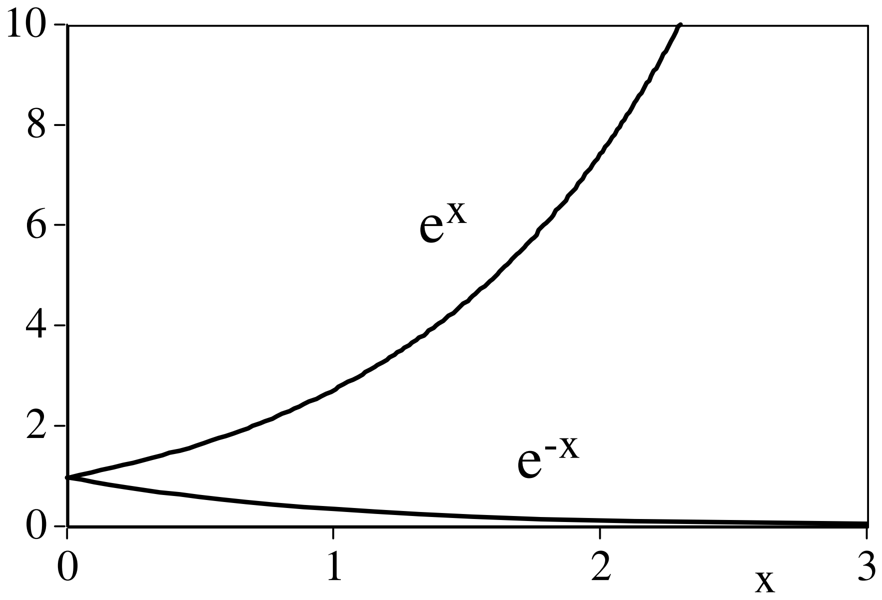
We normally think of integer exponents i.e. e^0, e^1, e^2, e^3..but exponents can have non-integer values. We have already met this in special cases.

e.g. $e^{1/2} = \sqrt{e}$ or $e^{2/3} = (\sqrt[3]{e})^2$

It is easy to calculate e^x for negative values of x from the rules of exponents that we already know.

$$e^{-x} = \frac{1}{e^x}$$

Calculators can calculate e^x for all values of x



e^x starts off at 1 and rapidly increases towards infinity.

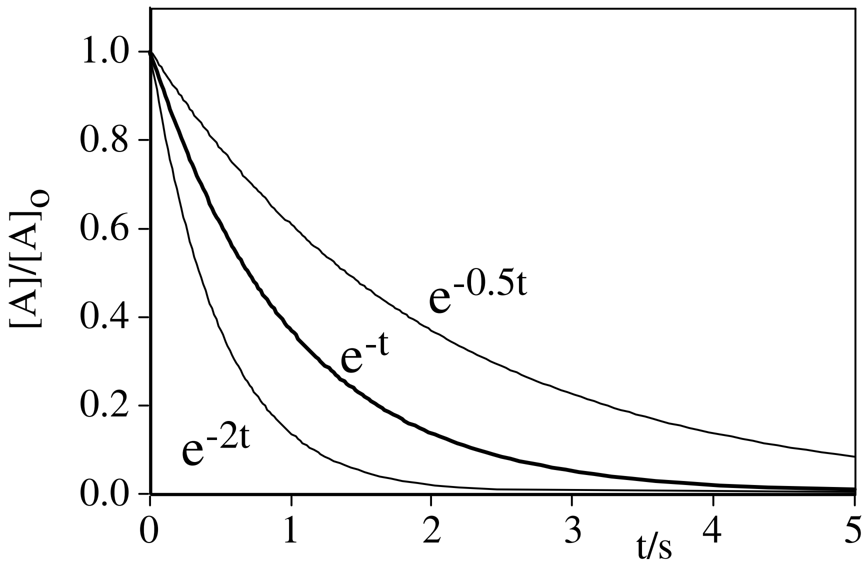
e^{-x} starts off at 1 and rapidly drops towards zero.

First Order reactions

A $\Longrightarrow$ B with rate constant k s^{-1}.

$$\frac{[A]}{[A]_o} = e^{-kt}$$

The concentration of A falls exponentially with time.



The rules for manipulating exponentials are just the ones we know already

$e^a\, e^b = e^{a+b}$ $e^{-a} = \frac{1}{e^a}$ $\frac{e^a}{e^b} = e^{a-b}$

$(e^a)^b = e^{a \times b}$ $e^0 = 1$

Practice Exercise 14

Evaluate

(a) e^3 (b) e^{-3} (c) e^3e^{-3} (d) $\dfrac{1}{e^{-3}}$

Simplify

(a) $\dfrac{e^{3x}}{e^{6x}}$ (b) $(e^{-3y})^2$

(c) $e^{x^2}\ e^{-2x+1}$ (d) $\dfrac{e}{e^{(x+1)}}$

An approximation to e^x when x is small is: $e^x \approx 1 + x + \dfrac{x^2}{2}$

Fill in the following table (to 4 decimal places)

x	1 + x	$1 + x + \dfrac{x^2}{2}$	e^x
0.5			
0.3			
0.1			
0.05			

What is the percentage error for x = 0.3 ?

Logarithms- base 10

$\log(x)$, $\log_{10}(x)$

Logarithms are just the inverse of exponentiation. It is the value of the exponent required to represent a number as a power of 10.

So if $y = 10^x$
then $x = \log(y)$

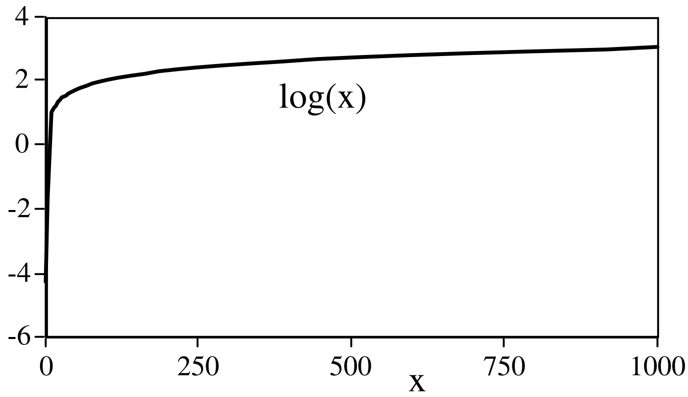
y	exponent form	log(y)
10	10^1	1
100	10^2	2
0.1	10^{-1}	–1
0.01	10^{-2}	–2

Any positive number can be represented in exponent form

y	exponent form	log(y)
73	$10^{1.8633}$	1.8633
9999	$10^{3.999957}$	3.999957
5.78×10^3	$10^{3.7619}$	3.7619
0.0234	$10^{-1.6308}$	–1.6308
1.1×10^{-4}	$10^{-3.9586}$	–3.9586

A special cases: $\log_{10}(1) = 0$ since $10^0 = 1$, $\log_{10}(10) = 1$ since $10^1 = 10$

It is impossible to take logarithms of negative numbers (at least without getting something called a complex number). Remember 10^{-3} is not negative -it's a small positive number.`



pH measurement

The most common use of logarithms in chemistry is the pH scale for acidity.

$$pH = -\log_{10}\left(\frac{[H^+]}{M}\right)$$, where M = standard molarity of 1 mol dm^{-3}.

Strong acids dissociate completely so the hydrogen ion concentration is easy to calculate.

10^{-3} M HCl	$[H+] = 10^{-3}$ M	$pH = -\log_{10}[10^{-3}] = 3$
10^{-4} M H_2SO_4	$[H+] = 2\times 10^{-4}$ M	$pH = -\log_{10}[2\times 10^{-4}] = 3.699$

What is the $[H^+]$ of an acid with pH = 4.6?

$$-\log_{10}\left(\frac{[H^+]}{M}\right) = 4.6$$

$$\log_{10}\left(\frac{[H^+]}{M}\right) = -4.6$$

$$[H^+] = 10^{-4.6}\ M = 2.511\times 10^{-5}\ \text{mol dm}^{-3}$$

Natural logarithms - ln(x) or Ln(x)

These are just the inverse of the exponential function

So if $y = e^{x}$
then $x = \ln(y)$ (special cases $\ln(1) = 0$, $\ln(e) = 1$)

Natural logarithms arise frequently in mathematics so scientific calculators always have buttons for ln(x) and e^{x}.

Properties of logarithms

We derive all the rules of logarithms from the rules for exponents

$x = 10^{a}$ then $a = \log_{10}(x)$
$y = 10^{b}$ and $b = \log_{10}(y)$

$xy = 10^{a} \times 10^{b} = 10^{a+b}$
(from the rules for exponents)
so
$\log_{10}(xy) = \log_{10}(10^{a+b}) = a + b$

hence
$\mathbf{\log_{10}(xy) = \log_{10}(x) + \log_{10}(y)}$

$\log_{10}(x^{a})$

express x in powers of 10

$x = 10^{p}$ so $p = \log_{10}(x)$

so
$x^{a} = (10^{p})^{a} = 10^{ap}$

hence
$\mathbf{\log_{10}(x^{a})} = \log_{10}(10^{ap}) = ap = \mathbf{a \log_{10}(x)}$

$\log_{10}(10^{x}) = x$	$\ln(e^{x}) = x$
$\log_{10}(x^{a}) = a \log_{10}(x)$	$\ln(x^{a}) = a \ln(x)$
$\log_{10}(xy) = \log_{10}(x) + \log_{10}(y)$	$\ln(xy) = \ln(x) + \ln(y)$
$\log_{10}(x/y) = \log_{10}(x) - \log_{10}(y)$	$\ln(x/y) = \ln(x) - \ln(y)$
$\log_{10}(1/x) = -\log_{10}(x)$	$\ln(1/x) = -\ln(x)$
$\log_{10}(x) = 0.434 \ln(y)$	$\ln(x) = 2.303 \log_{10}(x)$
$10^{\log_{10}(x)} = x$	$e^{\ln(x)} = x$

Examples

$\ln(3^{4}) = 4 \ln(3) = 4 \times 1.0986 = 4.3944$ {or equally $\ln(81) = 4.3944$}

$\ln(x^{3}) = 3 \ln(x)$

$\ln(e^3) = 3\ \ln(e) = 3$ (since $\ln(e) = 1$)

$\ln(\frac{x^3}{y^2}) = \ln(x^3) - \ln(y^2) = 3.\ln(x) - 2.\ln(y)$

$\ln(\frac{1}{e}) = -\ln(e) = -1$

if ln(x) = 2.2 what is x ? $x = e^{2.2} = 9.025$

Linear plots from exponentials

Arrhenius expression for a rate constant is:

$$k = Ae^{-E_a/RT}$$

hence

$$\ln(k) = \ln(A) + \ln(e^{-E_a/RT})$$

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \quad = \ln(A) - \frac{Ea}{R}\frac{1}{T}$$

so a plot of **ln(k)** vs $\mathbf{\frac{1}{T}}$ will be a straight line with gradient $-E_a/R$ and intercept of ln(A)

Practice Exercise 15

Evaluate **without** a calculator

(a) $\ln(e^4)$ **(b)** $\ln(e^{-2}) + \log_{10}(10^3)$ **(c)** $\ln\left(\frac{1}{e^{-3}}\right) + 10^{[\log_{10}(1/4)]}$

Simplify

(a) $\ln\left(\frac{x}{y^3}\right)$ **(b)** $\ln\left(\frac{a}{b^2}\right)^{3/2}$ **(c)** $\ln\left(\frac{e}{e^{(x+1)}}\right)$

Express the following interms of ln(3) and ln(2) (do not use a calculator)

(a) $\ln(6)$ **(b)** $\ln\left(\frac{1}{3}\right)$ **(c)** $\ln(8)$ **(d)** $\ln\left(\frac{3}{8}\right)$

What is the pH of 0.8 M HCl ? What would the pH be if it only 35% dissociated?

What is the $[H^+]$ of a solution with a pH = 7, and one with pH = – 0.4?

Practice Exercise 16

1 Calculate, ν, the frequency of light required to ionise a hydrogen atom.

$$\nu = \frac{m\, e^4}{8\, \varepsilon_o^2\, h^3}$$

$m = 9.109 \times 10^{-31}$ kg, $e = 1.602 \times 10^{-19}$ C,
$\varepsilon_o = 8.854 \times 10^{-12}\ J^{-1}\ C^2\ m^{-1}$, $h = 6.626 \times 10^{-34}$ J s

(Note: you will need to manipulate the powers of 10 by hand in order to get an answer from your calculator)

2 The Gibbs energy ΔG^o is related to the equilibrium constant, K, by

$\Delta G^o = - RT\ \ln(K)$ find an expression for K.

3 The Beer-Lambert law for light absorption when light passes through a sample is

$$I_t = I_o\ 10^{-\varepsilon CL}$$

I_t is the transmitted light intensity,
I_o is the incident intensity,
ε is the extinction coefficient, and L the path length

Find an expression for the concentration C.

4 Kohlrauch's law of the conductivity of a salt is

$$\Lambda_m = \Lambda^o{}_m - K\sqrt{c}$$

Λ_m is the molar conductivity,
$\Lambda^o{}_m$ is the molar conductivity at infinite dilution,
K is a constant

Find an expression for the concentration c.

5 A first order reaction A $\Longrightarrow$ X follows the integrated rate law

$$\ln\left(\frac{[A_o]}{[A_o] - [X]}\right) = kt$$ where $[A_o]$ is the initial concentration of A.

Find an expression for the product concentration, [X].

6 The wavelengths λ of the Balmer series of lines in the emission spectrum of Hydrogen obey the formula

$$\frac{1}{\lambda} = R_H\left(\frac{1}{4} - \frac{1}{n^2}\right)$$ where n = 3, 4, 5, ...

find an expression for n

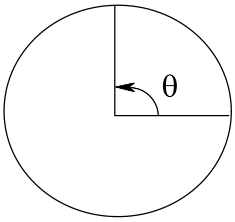
7 The rotational energy levels, E_n, for a diatomic molecule are given by

$E_n = B.n(n+1)$ n is the quantum number n = 0, 1, 2, 3...
and B is a constant

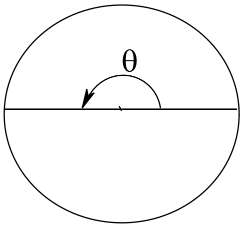
Derive a fomula for a transition, ΔE, between two levels with n = J+1 and n = J.

i.e. $\Delta E = E_{J+1} - E_J$.

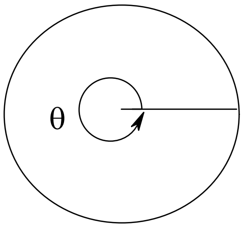
Degrees and Radians - trigonometry



$\theta = 90°$

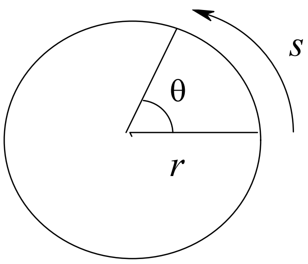


$\theta = 180°$



$\theta = 360°$

A more natural measure of angle is in RADIANS. Thus, in radians, the angle θ in the picture below, is given as the ratio of the arc length, s, to the radius, r.



i.e. $\theta = \dfrac{s}{r} = \dfrac{\text{arc length}}{\text{radius}}$

We know that the circumference of a circle = $2\pi r$

[and , in passing, we recall that the area of a circle $= \pi r^2$]

Therefore, for a full circle, $s = 2\pi r$, so the angle, in radians, corresponding to 360°, is given by

$$\theta = \frac{\text{arc length}}{\text{radius}} = \frac{2\pi r}{r} = 2\pi$$
$$\equiv 360°$$

i.e. $360° = 2\pi$ radians

Thus 1 radian = $(360/2\pi)°$, or $1° = 2\pi/360$ radians

This allows us to convert between radians and degrees. In general

$$\text{x radians} = \left(\frac{360 \times \text{x}}{2\pi}\right)^{\text{o}}$$

$$\text{x}° = \left(\frac{2\pi \times \text{x}}{360}\right) \text{radians}$$

Examples

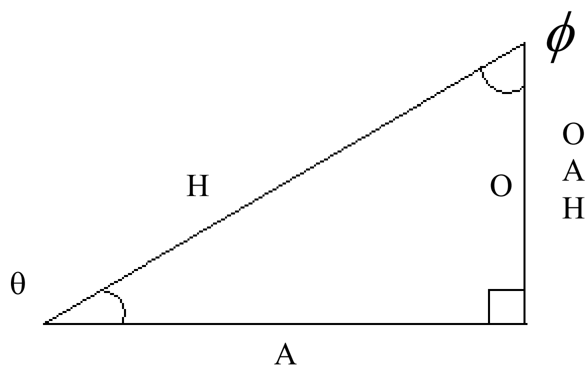
30° = ? radians

$$30° = \left(\frac{2\pi \times 30}{360}\right) \text{radians} = \frac{\pi}{6} \text{ radians}$$

$\frac{3\pi}{2}$ radians = ? °

$$\frac{3\pi}{2} \text{ radians} = \left(\frac{360 \times 3\pi}{2\pi \times 2}\right)^{\circ} = 270°$$

Triangles



O – Opposite
A – Adjacent
H – Hypontenuse

Length, H, of hypotenuse;

$H^2 = O^2 + A^2$ (Pythagoras)

or $H = \sqrt{O^2 + A^2}$

Given H and A we can work out O from

$O = \sqrt{H^2 - A^2}$

and finally, given H and O, we have

$A = \sqrt{H^2 - O^2}$

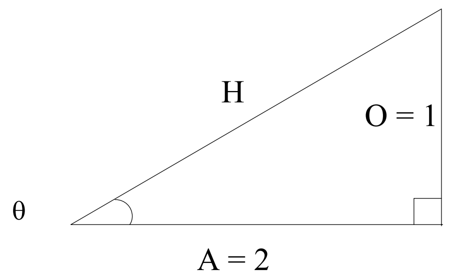
Finally we note that the third angle, ϕ, is given by $\boldsymbol{\theta + \phi + 90° = 180°}$ (sum of angles in a triangle)

Trigonometric functions

$$\sin\theta = \frac{O}{H} \qquad \cos\theta = \frac{A}{H} \qquad \tan\theta = \frac{O}{A}$$

[a mnemonic for this is: **s**ome **o**ld **h**ag **c**racked **a**ll **h**er **t**eeth **o**n **a**sparagus]

Example



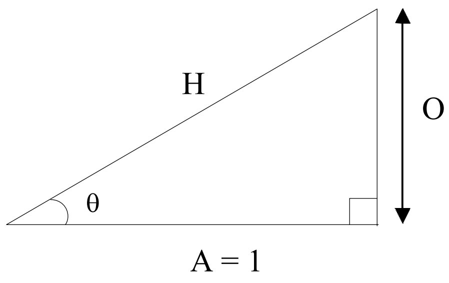
$H = \sqrt{2^2 + 1^2} = \sqrt{5}$

$$\sin\theta = \frac{O}{H} = \frac{1}{\sqrt{5}}$$

$$\cos\theta = \frac{A}{H} = \frac{2}{\sqrt{5}}$$

$$\tan\theta = \frac{O}{A} = \frac{1}{2}$$

Example



$\cos\theta = \frac{1}{3}$

a) H = ?

$$\cos\theta = \frac{A}{H} = \frac{1}{H} = \frac{1}{3}$$

Thus,

H = 3

b) *O* = ?

$$O = \sqrt{\left(H^2 - A^2\right)} = \sqrt{\left(3^2 - 1^2\right)} = \sqrt{8}$$

c) sin θ = ?

$$\sin\theta = \frac{O}{H} = \frac{\sqrt{8}}{3}$$

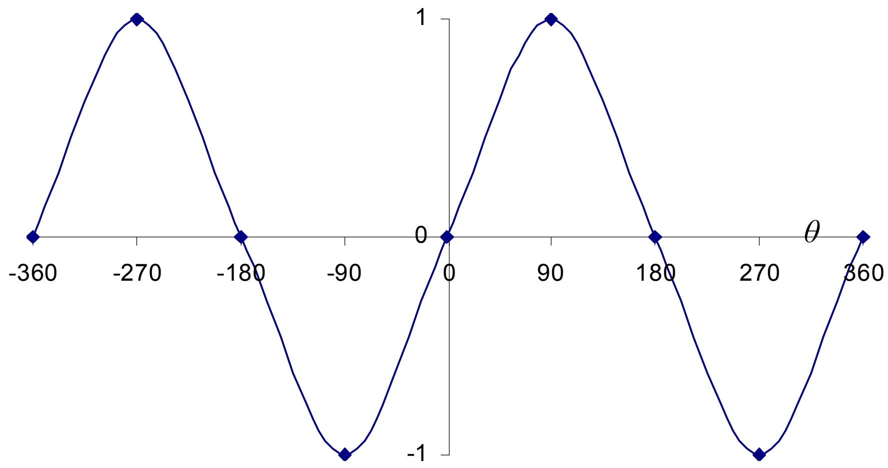
(d) tan θ = ?

$$\tan\theta = \frac{O}{A} = \sqrt{8}$$

More on Trigonometric Functions

sin θ, cos θ, and tan θ have values for any value of θ – positive, negative, small or large!

i) Sin θ



θ	sin θ
0	0
90° or $\frac{\pi}{2}$	1
180° or π	0
270° or $\frac{3\pi}{2}$	-1
360° or 2 π	0

This pattern repeats periodically

sin θ = 0, if θ = –360°, –180°, 0°, 180°, 360°
= –2π, – π, 0, π, 2 π (radians)

[In general: sin $\theta = 0$ if $\theta = \pm m\,\pi$; m integer]

Example

For what values of θ is sin θ =1?

From the graph or from the table, we know $\sin\theta = 1$ for $\theta = \pi/2$ or 90°.

As the graph repeats periodically, we can add or subtract any multiple of 2π to an angle θ and still get the same value for the sin function.

Thus $\sin\theta = 1$, if θ = …,–270°, 90°, 450°,…
= …, $-3\pi/2$, $\pi/2$, $5\pi/2$, … (radians)

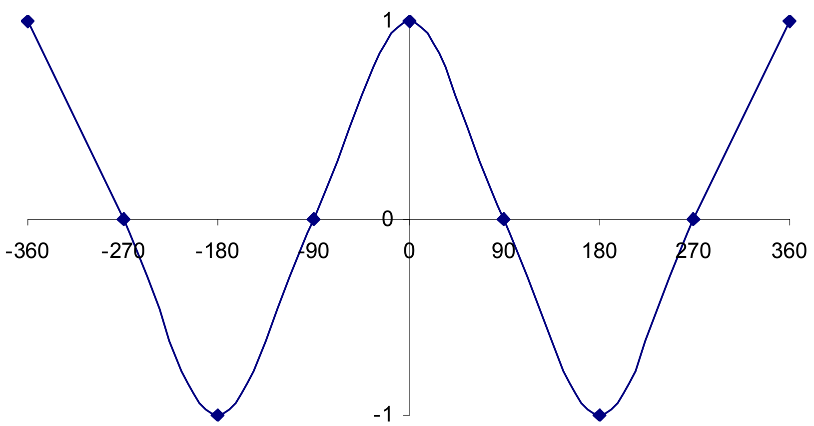
In general: $\sin\theta = 1$ if $\theta = \pi/2 \pm m\pi$; m integer

Finally, a useful fact is that if θ is small, $\sin\theta \approx \theta$ [θ in radians]

ii) cos θ

θ	**cos θ**
0	1
90° or $\frac{\pi}{2}$	0
180° or π	-1
270° or $\frac{3\pi}{2}$	0
360° or 2 π	1

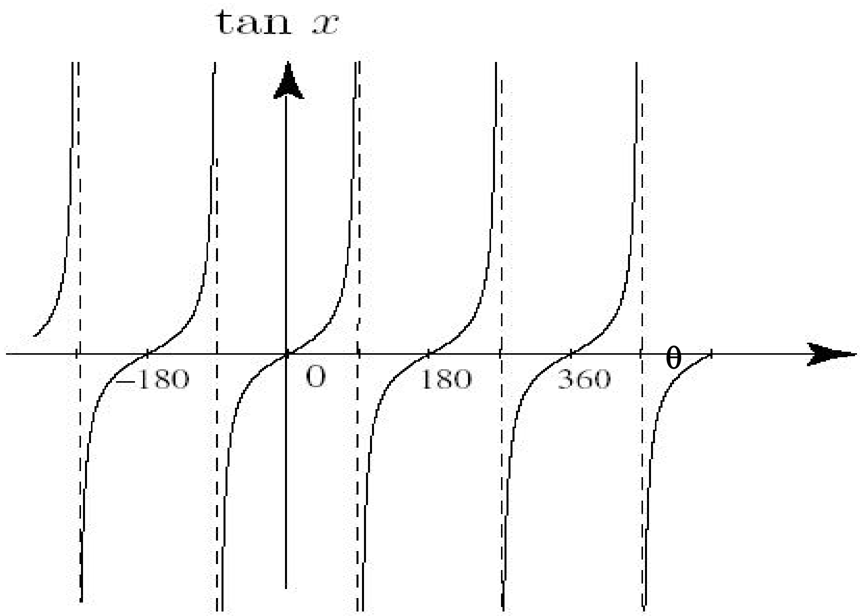
Again this pattern repeats periodically



$$\cos\theta = 0, \text{ if } \theta = \pm\frac{\pi}{2}, \pm\frac{3\pi}{2}, \pm\frac{5\pi}{2}, \text{etc}$$
$$\pm 90°, \pm 270°, \pm 450°, \text{etc}$$

If θ is small, $\cos\theta \approx 1 - \frac{\theta^2}{2}$ (θ in radians)

iii) Tan θ



$\tan\theta = 0$, if $\theta = \pm 0, \pm\pi, \pm 2\pi, \ldots$ (like $\sin\theta$)
(or $\pm 0°, \pm 180°, \pm 360°$, etc)

$\tan\theta = \pm\infty$, if $\theta = \pm\frac{\pi}{2}, \pm\frac{3\pi}{2}, \pm\frac{5\pi}{2}, \ldots$
(or $\pm 90°, \pm 270°, \pm 450°$, etc)

Small θ: $\tan\theta \approx \theta$ (θ in radians)

Inverse Trigonometric Functions

Suppose we are told $\sin\theta = 0.46$; what is the angle θ that gives this result?

Just as a matter of notation, we write

$\theta = \sin^{-1} 0.46 = \text{arc sin } 0.46$

[NOTE: $\sin^{-1} 0.46 \neq \frac{1}{\sin 0.46}$! We write: $\frac{1}{\sin x} = (\sin x)^{-1}$ to avoid confusion]

You can calculate arc sin (or $\sin^{-1}$) from tables or from calculators.

Similarly, you can calculate: arc cos or $\cos^{-1}$

arc tan or $\tan^{-1}$

Most calculators allow you to choose whether you want the answers in degrees or in radians –i.e. you can work in radian mode or degree mode.

Make sure you have chosen the appropriate option!

Examples

In radian mode, calculate:

arc sin (0.7)

arc cos (-0.3)

arc tan (1.0)

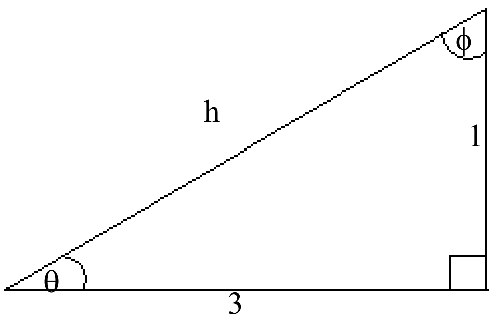
[Note: there are many angles, θ, such that $\tan\theta = 1.0$, e.g. $\theta = -\pi/4$, $\pi/4$, $5\pi/4$, etc. The calculator, however, simply returns one of these values. It may be that for your problem, you will need one of the other solutions!]

Practice Exercise 17

1 $45° = ?$ radians

2 $\frac{11}{6}\pi$ radians = ? degrees

3



Calculate h, $\cos\theta$, and $\tan\phi$. Do not evaluate the square root.

4 For what values of θ is $\cos\theta = 1$?

5 In degrees, calculate arc sin (–0.4), arc cos (0.8)

Test 3 Material

Differentiation I

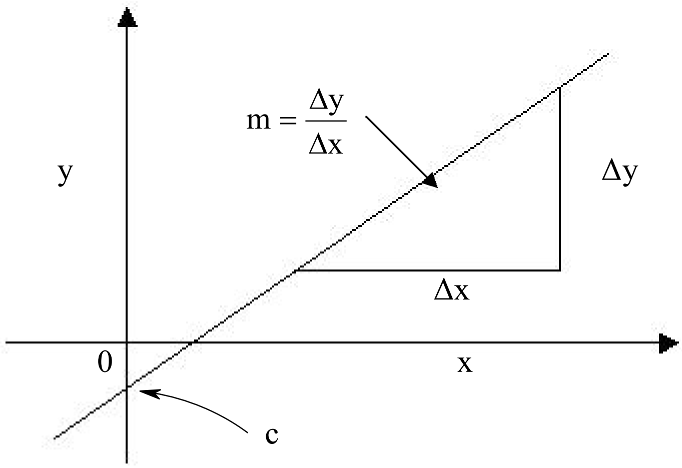
Straight Lines

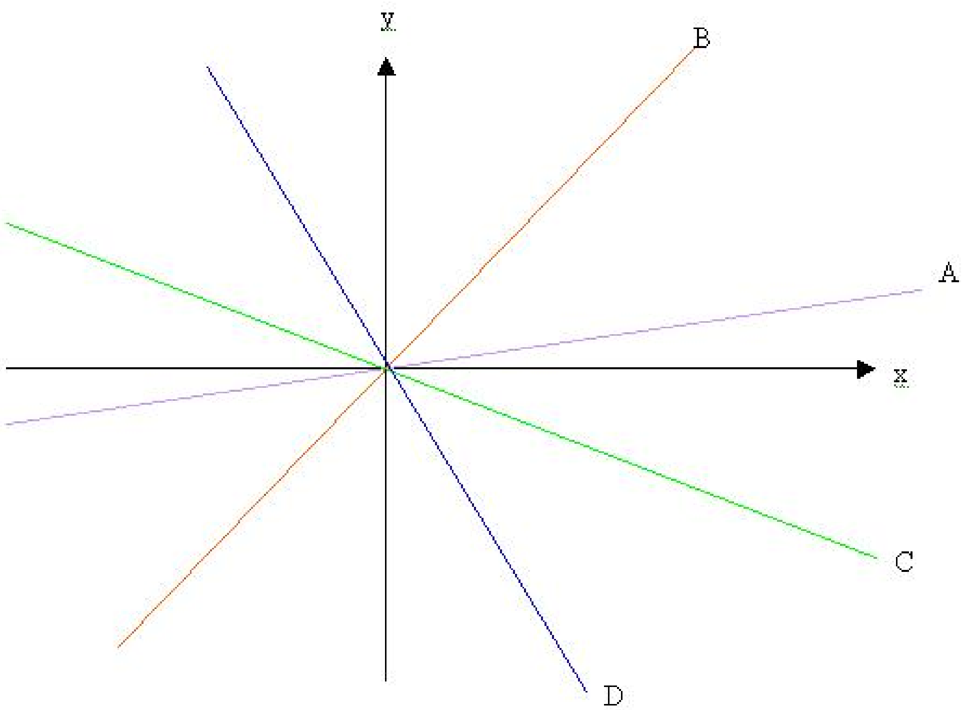
The equation for a straight line is:

$y = mx + c$

m = slope or gradient

c = intercept (value of y when x = 0)





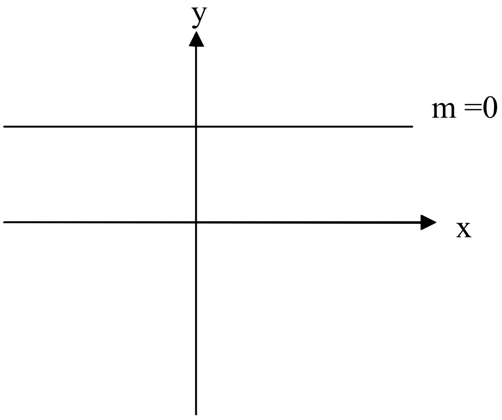
To gain a qualitative understanding of m, look at the lines above. We see:

Line A: Small, positive gradient, so a small, positive value of m

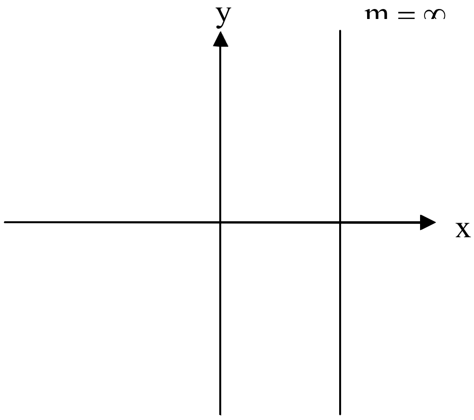
Line B: Large, positive value of m

Line C: Small negative value of m

Line D: Large negative value of m
Special cases are shown below.



Line with zero gradient



Line with infinite gradient

Physical example

A particle moves at constant velocity along a line

$$x = x_0 + vt$$

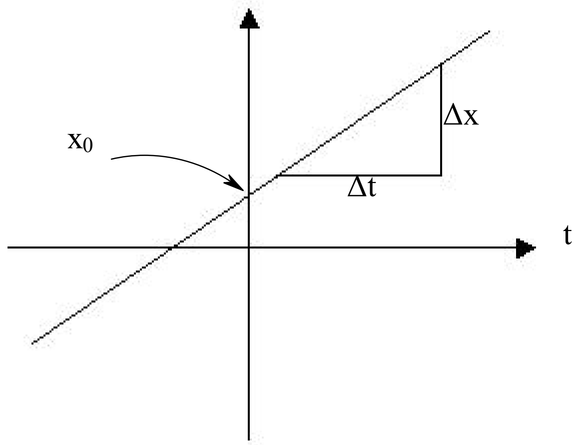
Position at time t

Starting Position

Velocity

Time

Thus a plot of x against t will give a straight line of gradient v and intercept x_0.



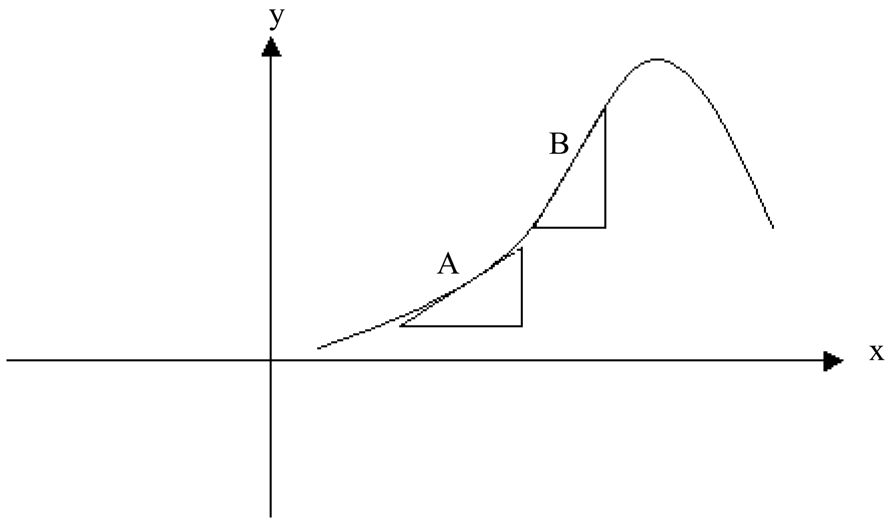
$$v = \text{gradient} = \frac{\Delta x}{\Delta t}$$

Velocity = rate of change of position with time

Non-Linear Graphs

For a straight line the gradient is the same everywhere. Thus in the previous picture, it does not matter where you draw your triangle – you always get the same gradient.

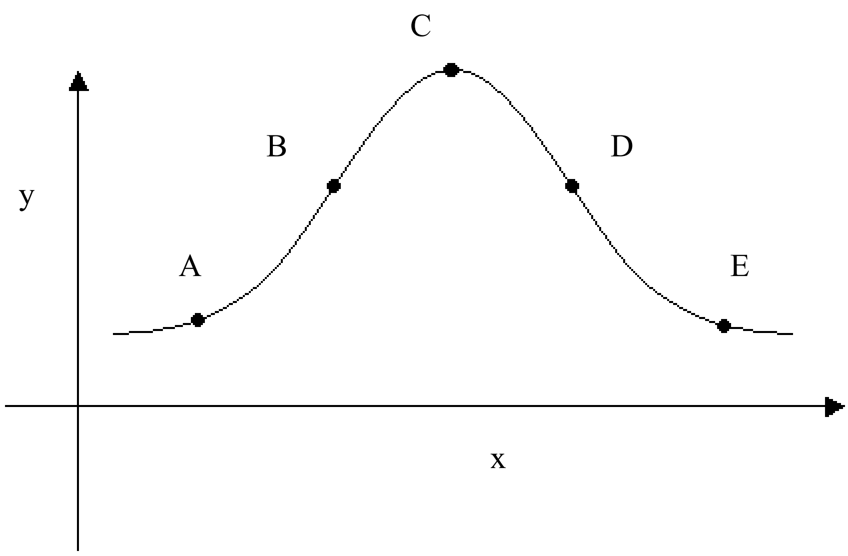
Now consider a *non-linear* graph.



For a *curve*, the gradient at a point is the gradient of the tangent line at that point.

Thus the gradient varies from point to point – i.e. the gradient is less at point A than it is at point B.

Look at the non-linear curve below and describe the gradients at points A to E.



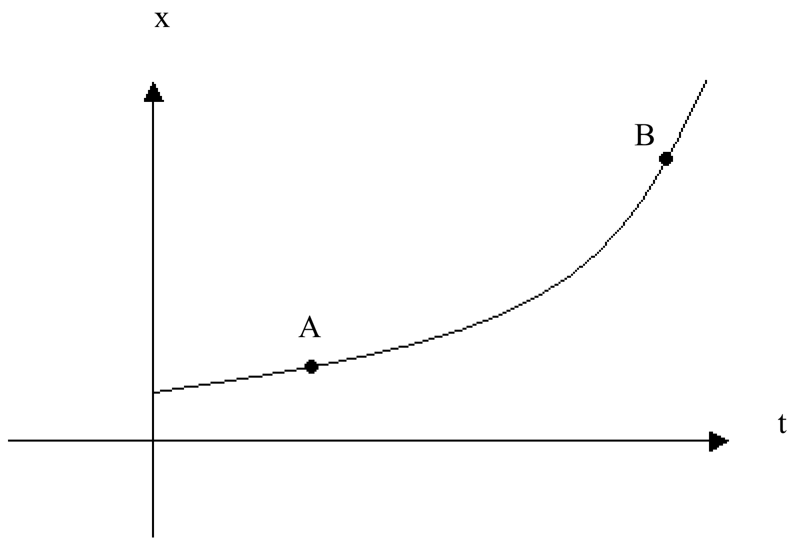
Point A: Small, positive gradient
Point B: Medium sized positive gradient
Point C: Zero gradient (Important! We return to this later when we discuss maxima and minima)
Point D: Medium sized negative gradient
Point E: Small, negative gradient.

As a matter of *notation*, the gradient of a curve (y vs. x) at position x is called $\frac{dy}{dx}$ (also called the *derivative* of y with respect to x).

The process of calculating $\frac{dy}{dx}$ is called *differentiation* and is part of a branch of mathematics called *calculus*.

Example

A particle moves along a line with a varying velocity. The curve of x vs t might look like the graph below.



At A – particle is moving slowly (small change of distance in time interval, Δt)

At B – particle is moving quickly (large change of distance in time interval, Δt)

The velocity at time t = gradient of curve at time t = $\frac{dx}{dt}$

If the velocity at time t is v, then the acceleration = $\frac{dv}{dt}$ (rate of change of velocity with time).

We now have a picture of what a derivative is - it is simply related to the slope of a curve. Suppose, though, we had a curve and we wanted to calculate the slope. For example we might wish to calculate the velocity of a particle at time t.

What do we do?
The answer is we have to follow some simple rules, which are justified in standard texts! The table of rules given below is to be memorised.

Rules of Differentiation

y	$\mathbf{\frac{dy}{dx}}$
c	0
mx + c	m
x^2	2x
x^3	$3x^2$
x^n	nx^{n-1}
e^x	e^x
e^{ax}	ae^{ax}
ln(x)	1/x
sin x	cos x
cos x	-sin x
sin ax	a cos ax
cos ax	-a sin ax

NB. c, m and a are constants – they do not depend on x

Examples

1) $y = x^4$ $\qquad \frac{dy}{dx} = ?$

This is of the form $y=x^n$ with n = 4

$$\therefore \frac{dy}{dx} = nx^{n-1} = 4x^{4-1}$$

$$\mathbf{= 4x^3}$$

2) $y = x^8$ $\qquad \frac{dy}{dx} = ?$

This is of the form $y=x^n$ with n = 8

$$\therefore \frac{dy}{dx} = nx^{n-1} = 8x^{8-1}$$
$$\mathbf{= 8x^7}$$

3) $y = \frac{1}{x^3}$ $\qquad \frac{dy}{dx} = ?$

$\frac{1}{x^3} = x^{-3}$ so this is of the form $y=x^n$ with n = -3

$$\therefore \frac{dy}{dx} = nx^{n-1} = -3x^{-3-1}$$
$$= -3x^{-4}$$
$$\mathbf{= \frac{-3}{x^4}}$$

4) $y = \frac{1}{x^5}$ $\qquad \frac{dy}{dx} = ?$

$\frac{1}{x^5} = x^{-5}$ so this is of the form $y=x^n$ with n = -5

$$\therefore \frac{dy}{dx} = nx^{n-1} = -5x^{-5-1}$$
$$= -5x^{-6}$$
$$\mathbf{= \frac{-5}{x^6}}$$

5) $y = \sqrt{x}$ $\qquad \frac{dy}{dx} = ?$

$\sqrt{x} = x^{1/2}$

so this is of the form $y=x^n$ with n = ½

$$\therefore \frac{dy}{dx} = nx^{n-1} = \frac{1}{2}x^{\frac{1}{2}-1}$$

$$= \frac{1}{2}x^{-1/2}$$

$$= \frac{1}{2x^{1/2}}$$

$$\mathbf{= \frac{1}{2\sqrt{x}}}$$

6) $y = x^{1/3}$ $\qquad \frac{dy}{dx} = ?$

This is of the form $y=x^n$ with $n = 1/3$

$$\therefore \frac{dy}{dx} = nx^{n-1} = \frac{1}{3}x^{1/3-1}$$

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

$$\mathbf{= \frac{1}{3x^{2/3}}}$$

7) $y = e^{-5x}$ $\qquad \frac{dy}{dx} = ?$

This is of the form $y = e^{ax}$ with $a = -5$

$$\therefore \frac{dy}{dx} = ae^{ax}$$

$$\mathbf{= -5e^{-5x}}$$

8) $y = e^{3x}$ $\qquad \frac{dy}{dx} = ?$

This is of the form $y = e^{ax}$ with $a = 3$

$$\therefore \frac{dy}{dx} = ae^{ax}$$

$$= \mathbf{3e^{3x}}$$

9) y = sin 2x $\qquad \frac{dy}{dx} = ?$

This is of the form y = sin ax with a = 2

$$\therefore \frac{dy}{dx} = a\cos ax$$

$$= \mathbf{2\cos 2x}$$

10) y = cos 5x $\qquad \frac{dy}{dx} = ?$

This is of the form y = cos ax with a = 5

$$\frac{dy}{dx} = -a\sin ax$$

$$= \mathbf{-5\sin 5x}$$

Thus using these rules is very straightforward! Much of the calculus needed in core chemistry is simply knowing these rules and being able to use them.

Sometimes, however, we need to do slightly more complicated things. We may need to differentiate sums of functions appearing in the table, or to differentiate these functions when multiplied by a constant. For this we need some extra, albeit obvious, rules.

Extra (obvious!) rules

1) Differentiate $y = 6x^2$

Here we have a function of x (i.e. x^2), multiplied by a constant (i.e. 6).

The rules say:

$$\frac{dy}{dx} = 6\frac{d(x^2)}{dx}$$

$$= 6 \times 2x$$

i.e. multiply derivative by the same constant

$$\mathbf{= 12x}$$

2) $y = 8e^{2x}$ $\frac{dy}{dx} = ?$

$$\frac{dy}{dx} = 8\frac{d(e^{2x})}{dx}$$

$$= 8 \times 2e^{2x}$$

$$\mathbf{= 16e^{2x}}$$

3) $y = e^x + \ln x$ i.e. y is a sum of functions

The rules say:

i.e. add derivatives

$$\frac{dy}{dx} = \frac{d(e^x)}{dx} + \frac{d(\ln x)}{dx}$$

$$\mathbf{= e^x + \frac{1}{x}}$$

4) $y = x^2 + \cos 6x$ $\frac{dy}{dx} = ?$

$$\frac{dy}{dx} = \frac{d(x^2)}{dx} + \frac{d(\cos 6x)}{dx}$$

$$\mathbf{= 2x - 6\sin 6x}$$

We now combine these rules!

5) $y = 3x^4 + 7e^{-x}$ $\qquad \frac{dy}{dx} = ?$

$$\frac{dy}{dx} = 3\frac{d(x^4)}{dx} + 7\frac{d(e^{-x})}{dx}$$

$$= 3 \times 4x^3 + 7 \times (-e^{-x})$$

$$\mathbf{= 12x^3 - 7e^{-x}}$$

6) $v = 2t + 5t^2$

$$\text{acceleration} = \frac{dv}{dt} = 2\frac{dt}{dt} + 5\frac{dt^2}{dt}$$

$$\mathbf{= 2 + 10t}$$

7) $[A] = [A]_0 e^{-k_1 t}$ $\qquad \frac{d[A]}{dt} = ?$

This is a chemical example – it describes how the concentration of a species A varies with time during a first order chemical reaction. $[A]_0$ and k_1 are constants.

$$\frac{d[A]}{dt} = [A]_0 \frac{de^{-k_1 t}}{dt}$$

$$\mathbf{= -k_1 [A]_0 e^{-k_1 t}}$$

8) $V = \frac{4}{3}\pi r^3$ $\qquad \frac{dV}{dr} = ?$

$$\frac{dV}{dr} = \frac{4\pi}{3}\frac{d(r^3)}{dr}$$

$$\mathbf{= 4\pi r^2}$$

9) $y = \ln(2x)$ $\qquad \frac{dy}{dx} = ?$

This looks hard – ln(2x) is not in the table!

However, we know ln 2x = ln2 + lnx

$$\therefore \frac{dy}{dx} = \frac{d(\ln 2)}{dx} + \frac{d(\ln x)}{dx}$$

$$= 0 + \frac{1}{x} \quad \mathbf{= \frac{1}{x}}$$

Remember: ln2 is just a number – i.e. a constant, c, so its derivative is zero

Special Rules

Two special rules with respect to differentiation which are commonly encountered in chemical problems are:

a) Differentiation of a Product.

If a function y = f(x) can be written as a product of two other functions, say u and v then the rule for product differentiation is:

$$\frac{\mathrm{dy}}{\mathrm{dx}} = \frac{\mathrm{d(uv)}}{\mathrm{dx}} = \mathrm{u}\frac{\mathrm{dv}}{\mathrm{dx}} + \mathrm{v}\frac{\mathrm{du}}{\mathrm{dx}}$$

For example if $y=x^2e^{3x}$, we can let $u = x^2$ and $v = e^{3x}$, therefore

$$\frac{dy}{dx} = x^2\frac{d(e^{3x})}{dx} + e^{3x}\frac{d(x^2)}{dx}$$
$$= 3x^2e^{3x} + 2xe^{3x} = (3x^2 + 2x)e^{3x}$$

b) The Chain Rule.

This rule is useful for functions such as y = f(x) = e^{ax^2} , where the exponent itself is a function of x.

In such cases we rewrite the function of x i.e f(x) as a function of a new function of u , f(u) where we have y = f(u(x)).

The rule states that in such cases:

$$\frac{dy}{dx} = \frac{dy}{du} \times \frac{du}{dx}$$

For example for the function above
y = f(x) = e^{ax^2}

we can write this as $y = e^u$, letting $u = ax^2$. Then using the rule above:

$$\frac{dy}{dx} = \frac{d(e^u)}{du} \times \frac{dax^2}{dx} = e^u \times 2ax$$
$$= e^{ax^2}2ax$$

Where u has been replaced by ax^2 in the exponential to give the final result solely in terms of x.

Practice Exercise 18

1 Calculate $\frac{dy}{dx}$ in the following cases:

a) $y = e^x$

b) $y = \ln x$

c) $y = \cos 7x$

d) $y = 2e^{-4x} + 3 \sin x$

e) $y = \frac{2}{x} + \frac{3}{x^6}$

f) $y = 7 + 8\sqrt{x} + \frac{9}{\sqrt{x}}$

g) $y = 2x^5 + \frac{3}{x^3} + 8$

h) $y = \ln(x^3) + 2x^{1/3} + \frac{2}{x^{1/3}}$ (Hint: What do you know about $\ln x^n$?)

i) $y = 4e^{5x} + 2 \sin 6x$

j) $y = \sin 2x \cos 3x$

k) $y = 3x^2 \ln(x)$

l) $y = \ln(x^3)$

2 Calculate the velocity ($v = \frac{dx}{dt}$) in the following:

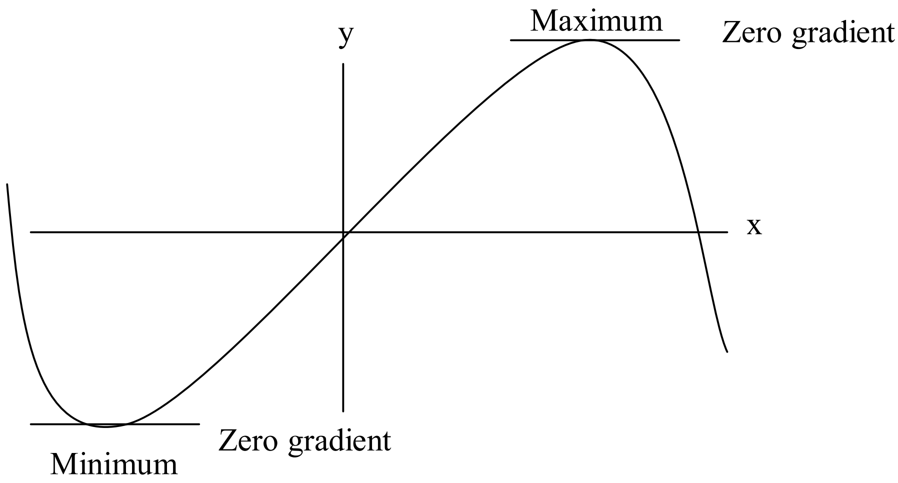
a) $x = 5e^{2t} + 2t^4$

b) $x = 2 \cos 3t + 3 \sin 5t$

c) $x = \ln(t^5)$

Differentiation II

Maxima and Minima.



The gradient is zero at a maximum or minimum. As a matter of notation, a point at which the gradient is zero is called a stationary point or a turning point. We can locate stationary points by finding out where dy/dx = 0.

Example

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

What is the minimum value of y?

$$\frac{dy}{dx} = 2x + 2$$

At a minimum: $\frac{dy}{dx} = 0$,

so $2x + 2 = 0$

and $\mathbf{x = -1}$

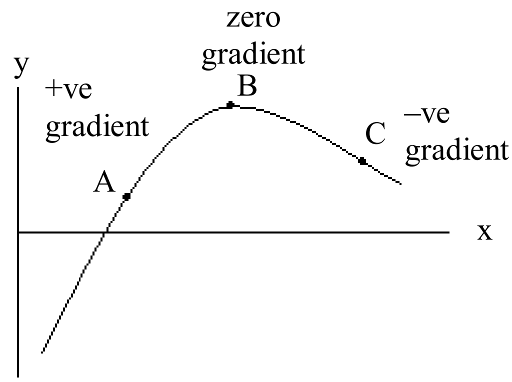
At the minimum

$y = (-1)^2 + 2 \times (-1) - 3$

$= 1 - 2 - 3$

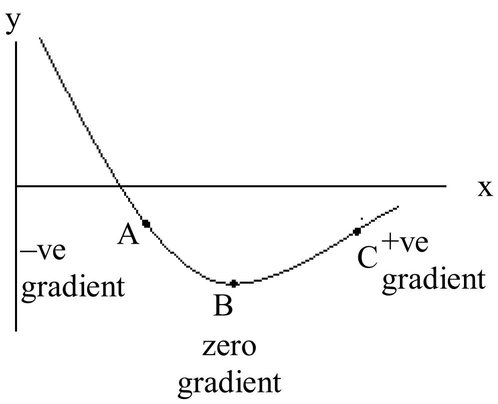
$\mathbf{y = -4}$

How do we know whether a turning point is a maximum or a minimum?



For a maximum, $\frac{dy}{dx}$ decreases with increasing x

(i.e. gradient goes from positive to negative).



For a minimum, $\frac{dy}{dx}$ increases with increasing x

(i.e. gradient goes from negative to positive).

The rate of change of y with x is called $\frac{dy}{dx}$

The rate of change of $\frac{dy}{dx}$ with x is thus $\frac{d}{dx}\left(\frac{dy}{dx}\right)$, which is written as $\frac{d^2y}{dx^2}$

It is called the second derivative of y with respect to x

If $\frac{dy}{dx}$ decreases as x increases, $\frac{d^2y}{dx^2} < 0$. A negative value of $\frac{d^2y}{dx^2}$ indicates a maximum

If $\frac{dy}{dx}$ increases as x increases, $\frac{d^2y}{dx^2} > 0$. A positive value of $\frac{d^2y}{dx^2}$ indicates a minimum.

This is the acid test:	**Maximum** $\frac{dy}{dx} = 0 \quad \frac{d^2y}{dx^2} < 0$
	Minimum $\frac{dy}{dx} = 0 \quad \frac{d^2y}{dx^2} > 0$

Examples

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

Show x = -1 corresponds to a minimum

$$\frac{dy}{dx} = 2x + 2$$

$$\frac{d^2y}{dx^2} = 2$$

2 > 0 (i.e. +ve)

Hence y is a minimum at $x = -1$

2) $y = x^3 - 12x + 4$

Find the two turning points and determine which is the maximum and which is the minimum.

$$\frac{dy}{dx} = 3x^2 - 12$$

At a stationary point, $\frac{dy}{dx} = 0$

$$\therefore 3x^2 - 12 = 0$$

$$x^2 = 4$$

$x = +2$ or $x = -2$

Thus there are two turning points. To determine their character we need to find $\frac{d^2y}{dx^2}$ at these points.

$$\frac{d^2y}{dx^2} = \frac{d(3x^2 - 12)}{dx} = 6x$$

At: $x = 2$; $\frac{d^2y}{dx^2} = 6 \times 2 = 12 > 0 \therefore x = 2$ is a <u>minimum</u>

At: $x = -2$; $\frac{d^2y}{dx^2} = 6 \times (-2) = -12 < 0 \therefore x = -2$ is a <u>maximum</u>

Partial Differentiation.

Often a physical quantity depends on two or more variables – e.g. the pressure of a one-component fluid, p, depends both on the temperature, T, and the molar volume, V_m.

Thus $p = p(T,V_m)$

For an ideal gas we know what this dependence is, i.e.

$$p = \frac{RT}{V_m}$$

In these cases we sometimes wish to know how the function changes if only one variable alters, all other variables remaining constant – e.g. how the pressure depends on temperature at constant volume.

Rather than talking about ordinary derivatives, such as we have just been discussing, we introduce the idea of a *partial derivative*. Because it is *partia*l as opposed to *full* diffferentiation we use a slightly different notation of ∂ (curly dee) as opposed to d.

Thus $\left(\frac{\partial p}{\partial T}\right)_{V_m}$ is the partial derivative of the pressure with respect to temperature, keeping the molar volume constant. Note the use of the curly dees!

Similarly, $\left(\frac{\partial p}{\partial V_m}\right)_T$ is the partial derivative of the pressure with respect to molar volume, keeping the temperature constant.

Calculating partial derivatives is no harder than calculating ordinary derivatives. You follow the same rules, treating the fixed variables as constants.

Let us do a few examples for practice:

Calculate $\left(\frac{\partial f}{\partial x}\right)_y$ and $\left(\frac{\partial f}{\partial y}\right)_x$ for the following functions, $f(x,y)$

(i) $f(x,y) = x^2 + y^3 + 2xy$

To calculate $\left(\frac{\partial f}{\partial x}\right)_y$ we use the normal rules of differentiation, treating y as a constant.

Thus

$$\left(\frac{\partial f}{\partial x}\right)_y = 2x + 0 + 2y$$
$$= 2x + 2y$$

To calculate $\left(\frac{\partial \mathrm{f}}{\partial \mathrm{y}}\right)_{\mathrm{x}}$ we use the normal rules of differentiation, treating *x* as a constant.

$$\left(\frac{\partial \mathrm{f}}{\partial \mathrm{y}}\right)_{\mathrm{x}} = 0 + 3\mathrm{y}^2 + 2\mathrm{x}$$
$$= 3\mathrm{y}^2 + 2\mathrm{x}$$

(ii) $f(x, y) = x\exp(y) + \frac{x}{y}$

$\left(\frac{\partial f}{\partial x}\right)_y = \exp(y) + \frac{1}{y}$ Again apply the normal rules, treating *y* as a constant.

$\left(\frac{\partial f}{\partial y}\right)_x = x\exp(y) - \frac{x}{y^2}$ This time take *x* as constant.

INTEGRATION

Suppose we are told:

$\frac{dy}{dx} = 3x^2$ and are asked to find **y**.

This procedure, the reverse activity to differentiation, is called integration.

In chemistry we use integration in kinetics and thermodynamics.

For example, if we know the velocity (dx/dt) we use integration to calculate the distance travelled.

Example

Constant velocity, $v = 2\ ms^{-1}$.

How far does a particle move in 1 second??

$\Delta x = 2$ m

How far does the particle move in time t?

$\Delta x = 2\ t$

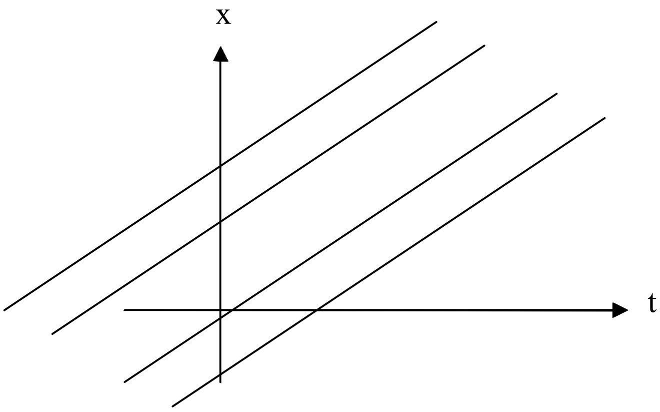
What is the position of the particle at time t? The general answer is

$x = x_0 + vt$

where x_0 is the starting position. This could be anything – we cannot calculate it! In calculus speak, x_0 is called the constant of integration.

Check

Given $x = x_0 + vt$, we can differentiate it to get $\frac{dx}{dt} = v$ – a result which isindependent of x_0. We can show the result graphically:



All lines are solutions of $\frac{dx}{dt} = v$, but have different values of x_0.

The notation used here is to write $x = \int v dt$ i.e. x is the integral of v with respect to time.

In general, if $y = \int f(x)dx$, then $\frac{dy}{dx} = f(x)$.

As in differentiation, we need rules to help us do these integrals. Again these rules must be learned.

Rules for Integration

f(x)	$\int f(x)dx$
m	mx+c
x	$\frac{1}{2}x^2 + c$
x^n	$\frac{x^{n+1}}{n+1} + c \; (n \neq -1)$
1/x	lnx+c
e^{ax}	$\frac{1}{a}e^{ax} + c$
sin (ax)	$-\frac{1}{a}\cos(ax) + c$
cos (ax)	$+\frac{1}{a}\sin(ax) + c$

c = constant of integration

Examples

1) $f(x) = x^2$, find $\int f(x)dx$

$$\int x^n dx = \frac{x^{n+1}}{n+1} + c$$

set n = 2, so

$$\int f(x)dx = \int x^2 dx$$

$$= \frac{x^{2+1}}{2+1} + c$$

$$= \mathbf{\frac{x^3}{3} + c}$$

2) f(x) = e^{2x}

$$\int e^{ax}\,dx = \frac{e^{ax}}{a} + c$$

here, a = 2, so

$$\int e^{2x}\,dx = \mathbf{=\frac{e^{2x}}{2} + c}$$

3) f(x) = cos4x

$$\int \cos(ax)\,dx = \frac{\sin(ax)}{a} + c$$

$$\therefore \int \cos(4x)\,dx = \frac{\sin 4x}{4} + c$$

Again we sometimes have to integrate sums of functions or a function multiplied by a constant. The rules here are obvious!

4) f(x) = $2\sqrt{x} + \frac{3}{x}$

$$\int f(x)\,dx = 2\int \sqrt{x}\,dx + 3\int \frac{1}{x}\,dx$$

i.e. we multiply the integrals by the required constants and add them!

a) $\sqrt{x} = x^{1/2}$;

$$\int x^n\,dx = \frac{x^{n+1}}{n+1} + c_1$$

n = ½;

$$\int x^{1/2}\,dx = \frac{x^{1+1/2}}{1+1/2} + c_1$$

$$= \frac{x^{3/2}}{(3/2)} + c_1$$

$$\mathbf{= \frac{2}{3}x^{3/2} + c_1}$$

b) $\int \frac{1}{x} dx = \ln x + c_2$

$$\therefore \int f(x)dx = 2 \times \left[\frac{2}{3}x^{3/2} + c_1\right] + 3 \times [\ln x + c_2]$$

$$\mathbf{= \frac{4}{3}x^{3/2} + 3\ln x + c}$$

(as c_1 and c_2 are arbitrary constant, $2c_1 + 3c_2$ combine to give a single arbitrary constant, c)

You only ever need <u>one</u> constant of integration!

5) $f(x) = 2e^{-x} + 3\sin(2x)$

$$\int f(x)dx = 2\int e^{-x}dx + 3\int \sin(2x)dx$$

$$= \frac{2e^{-x}}{(-1)} + \frac{3(-\cos 2x)}{2} + c$$

$$\mathbf{= -2e^{-x} - \frac{3}{2}\cos 2x + c}$$

Fixing the value of c.

Given extra information, we can calculate c.

Suppose we are told $\frac{dx}{dt} = 3t$ *and that* $x = 2$ when $t = 0$. (i.e. we are told the position at a certain time).

Standard integration gives

$$x = 3\int t\,dt = \frac{3t^2}{2} + c$$

But the constant, c, has to be such that x=2 when t=0. We therefore put x=2 and t=0 into the above equation and this fixes the value of c.

i.e. $2 = 0 + c$ so $c = 2$.

Thus the full solution is $\mathbf{x = \frac{3t^2}{2} + 2}$

This fits both the initial condition and gives the required value of dx/dt

Example

$\frac{dx}{dt} = 4e^t$; $x = 1$ when $t = 0$.

$$x = 4\int e^t dt = 4e^t + c$$

Now fix the value of c, by putting x=1 and t=0 into this equation.

$$1 = 4e^0 + c = 4 + c$$

Thus $\mathbf{c = -3}$

and the final solution is

$$\mathbf{x = 4e^t - 3}$$

We can now work out the value of x at any time, t, we wish. For example at t=1,
x = 4e – 3 = 7.873…. You will be asked questions like this in the computerised tests.

Differential Equations.

If $\frac{dy}{dx} = f(x)$

$y = \int f(x)dx$

Suppose $\frac{dy}{dx} = g(y)$? i.e. RHS involves y

To proceed:

$\int \frac{dy}{g(y)} = \int dx$ i.e. divide by g(y), multiply by dx, integrate

$= x$

Example

$$\frac{dy}{dx} = -2y$$

$$\therefore \int \frac{dy}{y} = -2\int dx = -2x$$

$$\therefore \mathbf{\ln y = -2x + c}$$

Differential equation example from reaction kinetics:

$\frac{d[A]}{dt} = -k_1[A]$ First order rate equation

$$\therefore \int \frac{d[A]}{[A]} = -k_1 \int dt$$

$$\therefore \ln[A] = -k_1 t + c$$

If we are told the initial concentration, we can find c

E.g. At $t = 0$, $[A] = [A]_0$

$$\therefore \ln[A]_0 = 0 + c = c$$

$$\therefore \ln[A] = -k_1 t + \ln[A]_0$$

$$\therefore \ln[A] - \ln[A]_0 = -k_1 t$$

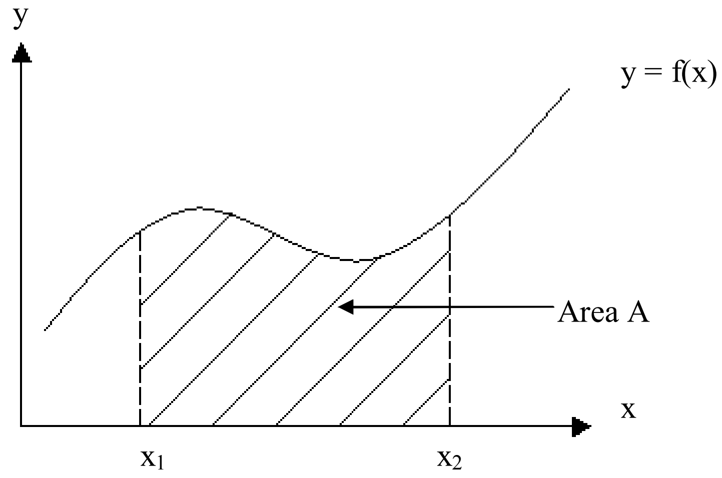
$$\therefore \ln\left\{\frac{[A]}{[A]_0}\right\} = -k_1 t$$

$$\therefore \frac{[A]}{[A]_0} = e^{-k_1 t}$$

$$\therefore \mathbf{[A] = [A]_0\, e^{-k_1 t}}$$

Definite integrals and areas under a curve.

Integration also corresponds to finding the area under a curve



$$A = \int_{x_1}^{x_2} f(x)dx$$

x_2 – upper limit
x_1 – lower limit

This is a definite integral

Example

1) $f(x) = x^2$; $x_1 = 0, x_2 = 1$

$$\therefore A = \int_0^1 x^2 dx$$

$$A = \left[\frac{x^3}{3} + c\right]_0^1$$

This means:

(a) Put the indefinite integral inside the square brackets.
(b) work out the value in brackets for the top value (i.e. x=1)
(c) work out the value in brackets for the bottom value (ie x= 0)
(d) work out (b)–(c) for final answer

i.e. x = 1 i.e. x = 0

$$A = \left\{\frac{1^3}{3} + c\right\} - \left\{\frac{0^3}{3} + c\right\}$$

$$A = \frac{1}{3}$$

Note: The arbitrary constant, c, cancels out. We can ignore "c" when calculating definite integrals.

2) $f(x) = e^{2x}$; $x_1 = 1, x_2 = 2$

$$A = \int_1^2 e^{2x}\,dx$$

$$= \left[\frac{e^{2x}}{2}\right]_1^2$$

$$= \left\{\frac{e^4}{2} + c\right\} - \left\{\frac{e^2}{2} + c\right\}$$

From now on we will not write down "c" at this step as they always cancel

$$= \mathbf{\frac{e^4}{2} - \frac{e^2}{2}}$$

Chemical Example

The work done (W.D) in reversibly changing the volume of a system from V_1 to V_2

$$= -\int_{V_1}^{V_2} p\,dv$$

Ideal gas: $p = \frac{nRT}{V}$

At constant temperature (isothermal)

$$\mathrm{W.D} = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

(nRT is a constant)

$$= -nRT\left[\ln V\right]_{V_1}^{V_2}$$

$$= -nRT\left\{\ln V_2 - \ln V_1\right\}$$

$$\mathbf{= -nRT\ln\left(\frac{V_2}{V_1}\right)}$$

Finally, we note: $\int_{x_1}^{x_2} f(x)dx = -\int_{x_2}^{x_1} f(x)dx$

Reversing the limits changes the sign of the definite integral.

Practice Exercise 19

1. Find the stationary (turning) points of

   $y = x^3 - 27x$

   and give the values of y at these points.

   Calculate $\frac{d^2y}{dx^2}$ and thus find whether the turning points are maxima or minima.

.

2. Calculate $\left(\frac{\partial f}{\partial x}\right)_y$ and $\left(\frac{\partial f}{\partial y}\right)_x$ in the following cases:

   a) $f(x,y) = x^3 + 2y^4 + x^2y^2$
   b) $f(x,y) = x\sin y + y\cos x + 3xy$

3. Integrate the following f(x):

   a) $f(x) = \frac{3}{x^2}$

   b) $f(x) = \frac{2}{\sqrt{x}}$

   c) $f(x) = 1 + 3x^2$

   d) $f(x) = 2e^{-x} + 3e^{-2x}$

4. Calculate x in the following cases:

   a) $\frac{dx}{dt} = \frac{2}{t}$; x = 2 when t = 1

   b) $\frac{dx}{dt} = 3 + 5t^3$; x = 0 when t = 0

5. In second order kinetics $\frac{d[A]}{dt} = -k_2[A]^2$

If $[A] = [A]_0$ at $t = 0$, show:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t$$

Practice Exercise 20

1 Calculate $\int f(x)dx$ in the following cases:

a) $f(x) = 6 + 2\sqrt{x} + \dfrac{3}{x^5}$

b) $f(x) = 2\cos(2x) + 3e^{3x} + 4x^{3/2}$

2 Calculate x in the following cases:

a) $\dfrac{dx}{dt} = \dfrac{3}{t} + 2t$; $x = 1$ when $t = 1$

b) $\dfrac{dx}{dt} = 2e^{-5t}$; $x = 1$ when $t = 1$

3 Calculate the following definite integrals:

a) $\displaystyle\int_{-1}^{1} \left[x^3 + x^5\right] dx$

b) $\displaystyle\int_{1}^{2} \left[e^{2t} + \frac{3}{t^2}\right] dt$

Practice Exercise Answers

Practice Exercise 1 – Answers

Expand the following expressions

$(x + 1)(x + 6)$	$x^2 + 6x + x + 6$ $x^2 + 7x + 6$
$(4x + 1)(2x + 2)$	$8x^2 + 8x + 2x + 2$ $8x^2 + 10x + 2$
$(x + 4)(x – 6)$	$x^2 - 6x + 4x – 24$ $x^2 – 2x – 24$
$(2x – 1)(3x + 2)$	$6x^2 + 4x – 3x – 2$ $6x^2 + x – 2$
$(2x - 1)(3x –2)$	$6x^2 – 4x – 3x + 2$ $6x^2 – 7x + 2$
$(x – 1)(–x + 6)$	$– x^2 + 6x + x – 6$ $– x^2 + 7x – 6$
$(–x –3)(–6x + 4)$	$6x^2 – 4x + 18x – 12$ $6x^2 + 14x – 12$
$(x + 1)^3$	$(x + 1)(x + 1)^2 = (x + 1)(x^2 + 2x +1)$ $x^3 + 2x^2 + x + x^2 + 2x + 1$ $x^3 + 3 x^2 + 3x + 1$
$(x + a)^3$	$(x + a)(x + a)^2 = (x + a)(x^2 + 2ax + a^2)$ $x^3 + 2ax^2 + xa^2 + ax^2 + 2a^2x + a^3$ $x^2 + (2a + a)x^2 + (a^2 + 2a^2)x + a^3$ $x^3 + 3ax^2 + 3a^2x + a^3$

Factorise the following expressions

$x^2 – 1$	$(x – 1)(x + 1)$

$$x^2 + 2x + 1 \qquad (x + 1)(x + 1) = (x + 1)^2$$

$$x^2 - 2x + 1 \qquad (x - 1)(x - 1) = (x - 1)^2$$

Practice Exercise 2 - Answers

Evaluate the following expressions

$\frac{1}{3} + \frac{1}{5}$ $\qquad$ $\frac{1\times 5 + 1\times 3}{3\times 5} = \frac{8}{15}$

$\frac{2}{5} - \frac{4}{9}$ $\qquad$ $\frac{2\times 9 - 4\times 5}{5\times 9} = \frac{18-20}{45} = -\frac{2}{45}$

$\frac{2}{3} \times \frac{4}{9}$ $\qquad$ $\frac{2\times 4}{3\times 9} = \frac{8}{27}$

$\frac{2}{3} \div \frac{4}{9}$ $\qquad$ $\frac{2}{3} \times \frac{9}{4} = \frac{2\times 9}{3\times 4} = \frac{18}{12} = \frac{6\times 3}{6\times 2} = \frac{3}{2}$

$\frac{2}{3x} + \frac{3}{y}$ $\qquad$ $\frac{2y + 3\times 3x}{3x\times y} = \frac{2y+9x}{3xy}$

$\frac{2}{3x} + \frac{3}{x}$ $\qquad$ $\frac{2x + 3\times 3x}{3x\times x} = \frac{2x+9x}{3x^2} = \frac{11x}{3x^2} = \frac{11}{3x}$

$\frac{1}{(x+2)} + \frac{1}{(x+3)}$ $\qquad$ $\frac{(x+3)+(x+2)}{(x+2)(x+3)} = \frac{2x+5}{(x+2)(x+3)}$

$(x+2) - \frac{6}{(x+3)}$ $\qquad$ $\frac{(x+2)}{1} - \frac{6}{(x+3)} = \frac{(x+2)(x+3)-6}{x+3}$

$$= \frac{x^2 + 3x + 2x + 6 - 6}{x+3}$$

$$= \frac{x^2 + 5x}{x + 3} = \frac{x(x+5)}{(x+3)}$$

Practice Exercise 3 – Answers

Rearrange the following expressions to obtain x

$x + 1 = 3$	$x = 2$ move 1 over
$-4x + 1 = 2$	$-4x = 1$ move 1 over $4x = -1$ multiply both sides by -1 $x = -\frac{1}{4}$ divide by 4
$\frac{(x+4)}{3} = 2$	$x + 4 = 6$ multiply by 3 $x = 2$ move 4 over
$(7x - 1) = 2(2x + 1)$	$7x - 1 = 4x + 2$ multiply bracket out $7x - 4x = 2 + 1$ move 4x and -1 over $3x = 3$ evaluate $x = 1$ divide by 3
$\frac{(2x+1)}{(3x-2)} = 1$	$2x + 1 = 3x - 2$ multiply by $3x - 2$ $2x - 3x = -2 - 1$ move 3x and +1 over $-x = -3$ $x = 3$
$(x - 1)(x + 6) = x^2$	$x^2 + 5x - 6 = x^2$ multiply brackets out $x^2 - x^2 + 5x - 6 = 0$ move x^2 over $5x = 6$ move 6 over $x = 1\frac{1}{5}$
$\frac{(2x-a)}{(y+b)} = 4$	$2x - a = 4(y + b)$ multiply by $(y + b)$ $2x = 4(y + b) + a$ move a across $x = \frac{4(y+b)+a}{2}$ divide by 2
$\frac{(2x-a)}{y} = \frac{x}{3} + \frac{3}{y}$	$\frac{(2x-a)}{y} = \frac{xy+9}{3y}$ RHS over common factor $3(2x - a) = xy + 9$ multiply by 3y $6x - 3a = xy + 9$ expand $6x - xy = 3a + 9$ move terms over

$x(6 - y) = 3(a + 3)$ common factors

$x = \frac{3(a+3)}{(6-y)}$ divide $(6 - y)$

Practice Exercise 4 – Answers

Rearrange the following expressions to obtain x

$(x + 1)^2 = 16$

$x + 1 = 4$ square root both sides
$x = 3$ move 1 over
but also
$x + 1 = -4$ negative square root
$x = -5$ move 1 over

$\sqrt{\dfrac{x}{y}} = a + b$

$\dfrac{x}{y} = (a + b)^2$ square both sides
$x = y(a + b)^2$ multiply by y

$\sqrt{-4x + 1} = y$

$-4x + 1 = y^2$ square both sides
$-4x = y^2 - 1$ move 1 over
$4x = 1 - y^2$ multiply by -1
$x = \dfrac{1 - y^2}{4}$ divide by 4

$\dfrac{1}{2}\, mx^2 = \dfrac{3}{2}\, kT$

$mx^2 = 3kT$ muliply by 2
$x^2 = \dfrac{3kT}{m}$ divide by m
$x = \pm\sqrt{\dfrac{3kT}{m}}$ square root

$\dfrac{1}{\sqrt{x}} = \dfrac{1}{a} + \dfrac{1}{b}$

$\dfrac{1}{\sqrt{x}} = \dfrac{b + a}{ab}$ RHS over common factor
$\sqrt{x} = \dfrac{ab}{a + b}$ invert both sides
$x = \left(\dfrac{ab}{a + b}\right)^2$ square both sides

In thermodynamics the Gibbs energy change for a reaction is given by

$\Delta G = \Delta H - T\Delta S$ find an expression for ΔS

$T\Delta S = \Delta H - \Delta G$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

The Van der Waals equation for a gas has the form

$\left(p + \dfrac{a}{V_m^2}\right)\left(V_m - b\right) = RT$ find an expression for p

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

$$p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

Practice Exercise 5 - Answers

What percentage is the first quantity of the second in the following?

(a) 27 of 54 **(b)** 0.15 of 0.37 **(c)** 61 of 48 **(d)** 17x of 51x

$\frac{27}{54} \times 100 = 50\%$ $\frac{0.15}{0.37} \times 100 = 40.54\%$ $\frac{61}{48} \times 100 = 127\%$ $\frac{17x}{51x} \times 100 = 33\%$

What value is represented by the following percentages?

(a) 23% of 41 **(b)** 150% of 0.3 **(c)** 2% of 10^{-21} **(d)** 25% of (4x + 12)

$\frac{23}{100} \times 41 = 9.43$ $\frac{150}{100} \times 0.3 = 0.45$ $\frac{2}{100} \times 10^{-21} = 2 \times 10^{-23}$ $\frac{25}{100} \times (4x+12) = \frac{1}{4} \times 4(x+3)$

$= (x+3)$

A distance is measured as 10.3 ±0.2 miles. What is the percentage error?

$$\frac{\pm 0.2}{10.3} \times 100 = \pm 1.94\%$$

A distance is measured as 5 miles ± 7%. What is the uncertainty in yards (1mile = 1760 yards)

5 miles = 5 × 1760 = 8800 yards. Uncertainty = $\frac{\pm 7}{100} \times 8800 = \pm 616$ yards

A fuel additive increases the engine performance from 36 mpg to 45 mpg, what is the percentage improvement?

increase = $\frac{45}{36} \times 100 = 125\%$ or an improvement of 25%

improvement = $\frac{45 - 36}{36} \times 100 = \frac{9}{36} \times 100 = 25\%$

Practice Exercise 6 - Answers

1. Express the following numbers in scientific notation (e.g. 3123 becomes 3.123×10^{3})

   (i) 52,200 $\quad 52{,}200 = 5.22\times10^{4}$

   (ii) 0.00025 $\quad 0.00025 = 2.5\times10^{-4}$

2. Evaluate the following, leaving the answer in terms of powers of 10.

   (i) $(2\times10^{-5})\times(3\times10^{2}) = 6\times10^{-5+2} = 6\times10^{-3}$,

   (ii) $\dfrac{4\times10^{-3}}{2\times10^{-5}} = 2\times10^{-3-(-5)} = 2\times10^{2}$,

   (iii) $\left(10^{-3}\right)^{-4} = 10^{(-3)\times(-4)} = 10^{12}$

3. (i) Kinetic energy = $\dfrac{1}{2}mv^{2}$, where m is a particle's mass and v its speed.

   What are the dimensions of kinetic energy (i.e. in terms of ℓ, m, t, etc) and its units in terms of kg, m (metres) and s (seconds)?

   Dimensions of speed are $\ell\, t^{-1}$, so dimensions of kinetic energy are $m(\ell\, t^{-1})^{2} = m\,\ell^{2}t^{-2}$

   Units are kg m^{2} s^{-2} (equivalent to J)

   (ii) Pressure= force/area.

   What are the dimensions of pressure (i.e. in terms of ℓ, m, t, etc) and its units in terms of kg, m (metres) and s (seconds)?

   Dimensions of force are $m\,\ell\, t^{-2}$ and dimensions of area are ℓ^{2}. Hence dimensions of pressure are $m\,\ell\, t^{-2}/\,\ell^{2} = m\,\ell^{-1}t^{-2}$

   Hence units are kg m^{-1} s^{-2} (equivalent to Pa)

Practice Exercise 7 – Answers

1. From the equation $\Delta E = hc\bar{\nu}$, work out the units of $\bar{\nu}$, given that ΔE is in J, h is in J s and c is in m s^{-1}.

$$\bar{\nu} = \frac{\Delta E}{hc}\text{; units of } \bar{\nu} = \frac{\text{J}}{\text{Js} \times \text{ms}^{-1}} = \text{m}^{-1}$$

2. (i) What is 8 pm^3 in m^3?

$$8\text{pm}^3 = 8 \times \left(\frac{\text{pm}^3}{\text{m}^3}\right) \times \text{m}^3 = 8 \times \left(\frac{\text{pm}}{\text{m}}\right)^3 \times \text{m}^3 = 8 \times \left(\frac{10^{-12}\,\text{m}}{\text{m}}\right)^3 \times \text{m}^3 = 8 \times 10^{(-12)\times 3}\,\text{m}^3$$
$$= 8 \times 10^{-36}\,\text{m}^3$$

(ii) What is 4 ms^2 in s^2?

$$4\text{ms}^2 = 4 \times \left(\frac{\text{ms}^2}{\text{s}^2}\right) \times \text{s}^2 = 4 \times \left(\frac{\text{ms}}{\text{s}}\right)^2 \times \text{s}^2 = 4 \times \left(\frac{10^{-3}\,\text{s}}{\text{s}}\right)^2 \times \text{s}^2 = 4 \times 10^{(-3)\times 2}\,\text{s}^2$$
$$= 4 \times 10^{-6}\,\text{s}^2$$

(iii) What is 4 μg in kg?

$$4\mu\text{g} = 4 \times \left(\frac{\mu\text{g}}{\text{kg}}\right) \times \text{kg} = 4 \times \left(\frac{10^{-6}\,\text{g}}{10^3\,\text{g}}\right) \times \text{kg} = 4 \times 10^{-9}\,\text{kg}$$

3. What is

(i) 2.0 cm^{-1} in m^{-1}?

$$2.0\text{ cm}^{-1} = 2.0 \times \left(\frac{\text{cm}^{-1}}{\text{m}^{-1}}\right) \times \text{m}^{-1} = 2.0 \times \left(\frac{\text{cm}}{\text{m}}\right)^{-1} \times \text{m}^{-1} = 2.0 \times \left(\frac{10^{-2}\,\text{m}}{\text{m}}\right)^{-1} \times \text{m}^{-1}$$

$$= 2.0 \times 10^2\,\text{m}^{-1}$$

(ii) 4.0 ms^{-2} in s^{-2} ?

$$4.0\ ms^{-2} = 4.0\times\left(\frac{ms^{-2}}{s^{-2}}\right)\times s^{-2} = 4.0\times\left(\frac{ms}{s}\right)^{-2}\times s^{-2} = 4.0\times\left(\frac{10^{-3}s}{s}\right)^{-2}\times s^{-2}$$

$$= 4.0\times10^{6}s^{-2}$$

(iii) 3.0 mmol cm^{-3} in mol dm^{-3} ?

$$3.0mmolcm^{-3} = 3.0\times\left(\frac{mmolcm^{-3}}{moldm^{-3}}\right)\times moldm^{-3} = 3.0\times\left(\frac{mmol}{mol}\right)\times\left(\frac{cm}{dm}\right)^{-3}\times moldm^{-3}$$

$$= 3.0\times\left(\frac{10^{-3}mol}{mol}\right)\times\left(\frac{10^{-2}m}{10^{-1}m}\right)^{-3}\times moldm^{-3}$$

$$= 3.0\times10^{-3}\times\left(10^{-1}\right)^{-3} moldm^{-3}$$

$$= 3.0moldm^{-3}$$

4. What is:

(i) 3 cm μs^{-2} in m s^{-2} ?

$$3\,cm\,\mu s^{-2} = 3\left(\frac{cm}{m}\right)\left(\frac{\mu s}{s}\right)^{-2} m\,s^{-2} = 3\times10^{-2}\times\left(10^{-6}\right)^{-2} m\,s^{-2} = 3\times10^{-2}\times10^{12}\,m\,s^{-2}$$

$$= 3\times10^{10}\,m\,s^{-2}$$

(ii) 2 mm^3 ns^{-1} in m^3 s^{-1} ?

$$2\,mm^3\,ns^{-1} = 2\left(\frac{mm}{m}\right)^3\left(\frac{ns}{s}\right)^{-1} m^3\,s^{-1} = 2\times\left(10^{-3}\right)^3\times\left(10^{-9}\right)^{-1} m^3\,s^{-1}$$

$$= 2\times10^{-9}\times10^{9}\,m^3\,s^{-1} = 2\,m^3\,s^{-1}$$

Practice Exercise 8 – Answers

1. Calculate:

(i) ΔA from $\Delta A = \Delta U - T\Delta S$, where $\Delta U = 3.0$ kJ, $T = 100$ K and $\Delta S = 8.0$ J K^{-1}

You can either work in J or kJ, but you cannot mix them up! Working in J, we have

$$\Delta A = \left(3.0 \times 10^3 - 100 \times 8.0\right) \text{J} = (3000 - 800)\,\text{J} = 2200\,\text{J}.$$

Alternatively the answer can be $\Delta A = 2.2$ kJ.

(ii) E from $E = hcB$, where $h = 6 \times 10^{-34}$ J s, $c = 3 \times 10^8$ m s^{-1} and $B = 5$ cm^{-1}.

Here you must not mix up m and cm! If we work in m, then $B = 5 \times 10^2\ \text{m}^{-1}$, so

$$E = \left(6 \times 10^{-34} \times 3 \times 10^8 \times 5 \times 10^2\right) \text{J} = 90 \times 10^{-24}\ \text{J} = 9 \times 10^{-23}\ \text{J}$$

2. Kinetic data:

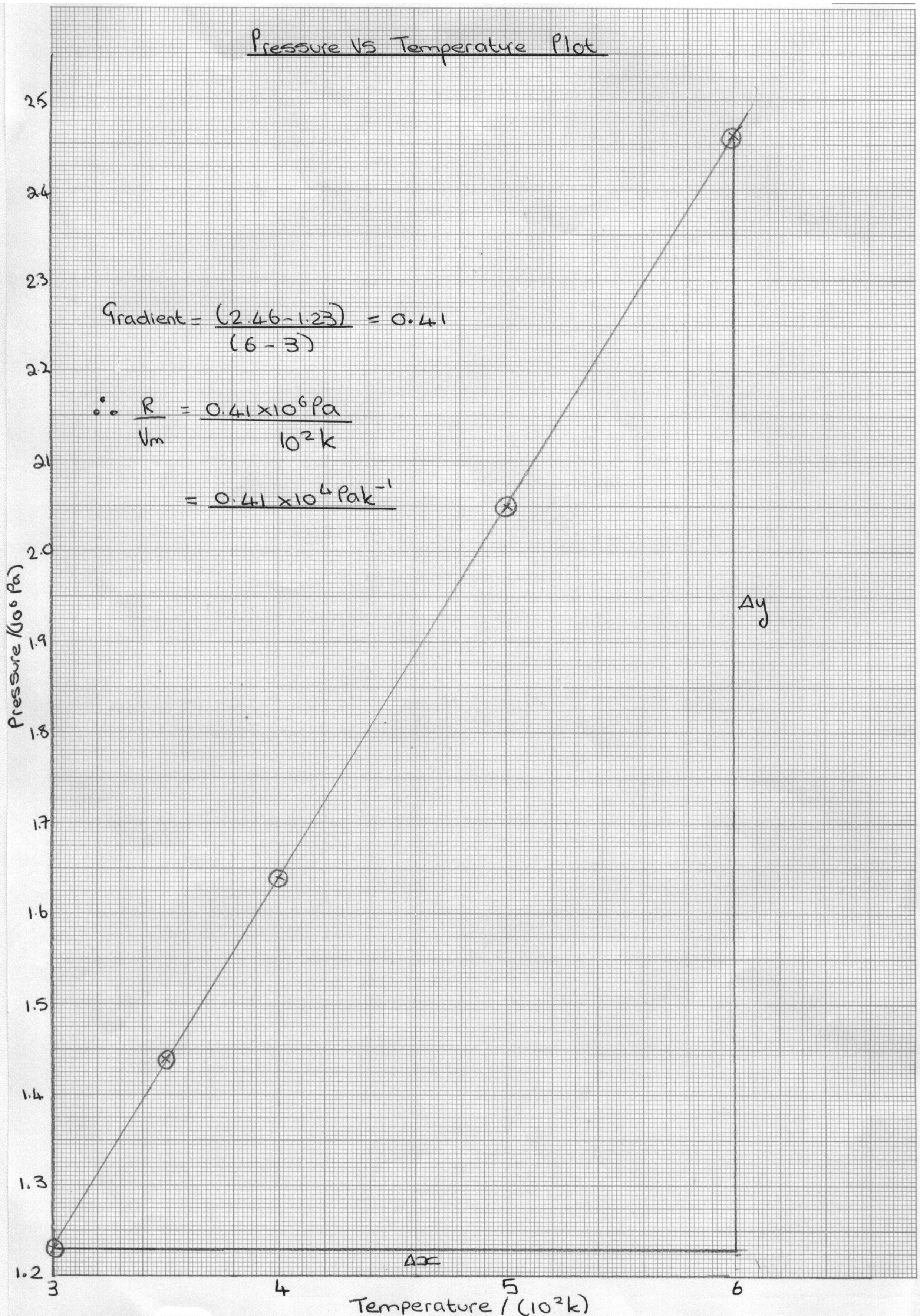
Time / (10^2 s)	0	1	**3**	7	13
Concentration / (10^{-3} mol dm^{-3})	10	8.5	**2.83**	1.72	0.96

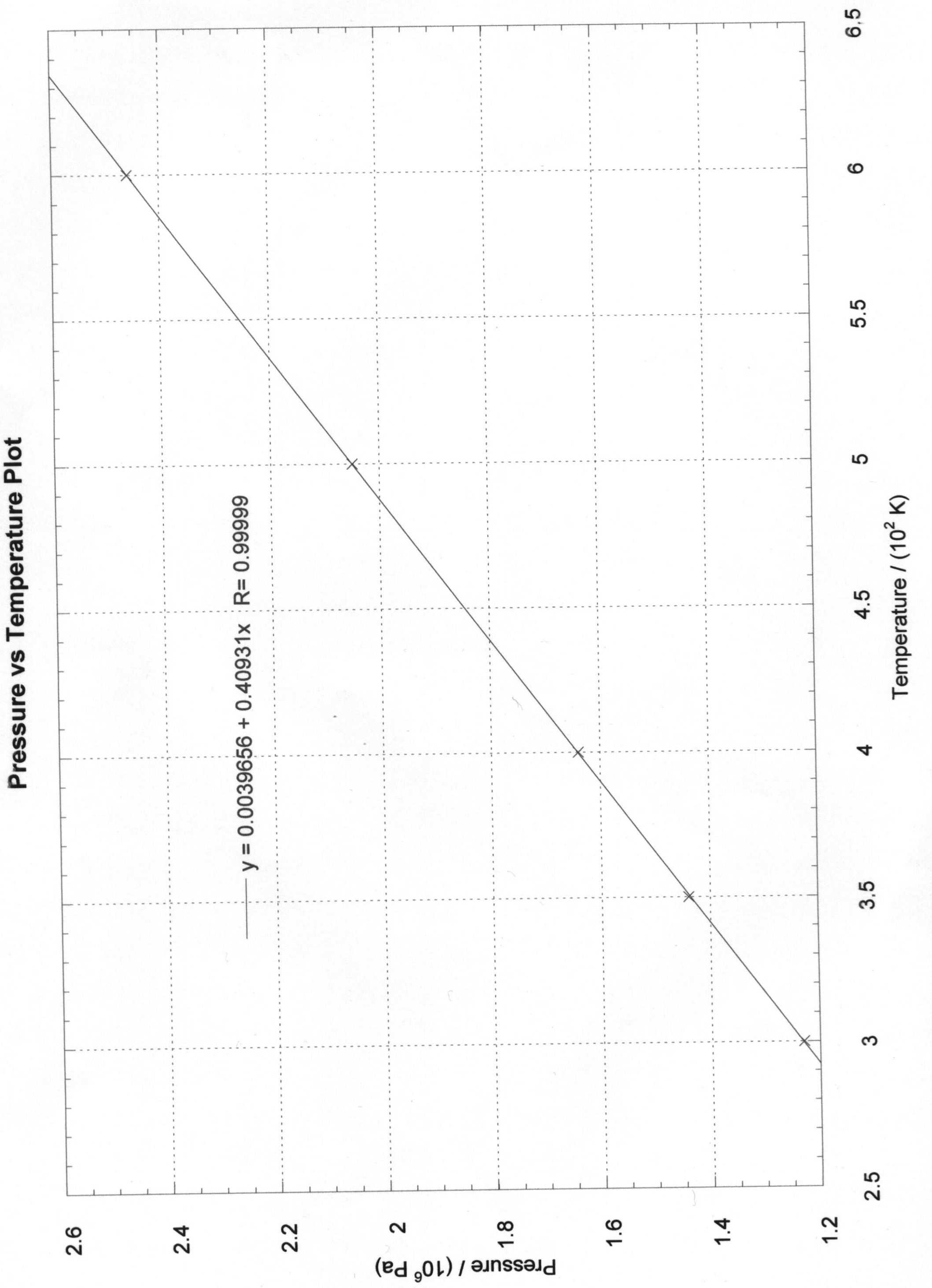
What time and what concentration correspond to the numbers in bold?

Time / (10^2 s) = 3;
Concentration / (10^{-3} mol dm^{-3}) = 2.83;

Time = 3×10^2 s
Concentration = 2.83×10^{-3} mol dm^{-3}

Practice Exercise 9 – Answers





2. The intercept of the graph, c, is given by

$$c = y - mx$$
$$c = 3.0 - 2.5 \times 2.0 = -2.0$$

We have $c = r_0/(10^3 \text{ m})$, so
$$r_0 = -2.0 \times 10^3 \text{ m}$$

Practice Exercise 10 – Answers

1.

$$\overline{K} = \frac{2.0 + 7.0 + 3.}{3} = 4.0$$

$$\sigma_K = \sqrt{\frac{(2.0-4.0)^2 + (7.0-4.0)^2 + (3.0-4.0)^2}{3 \times 2}} = \sqrt{\frac{14}{6}} = 1.5$$

$\therefore K = 4.0 \pm 1.5$

2. (i) C = 4.0 – 3.0 = 1.0; $\sigma_C^2 = \sigma_A^2 + \sigma_B^2 = 0.25;\quad \sigma_C = 0.5$

$\therefore C = 1.0 \pm 0.5$

(ii) C = 4.0 + 3.0 = 7.0; $\sigma_C^2 = \sigma_A^2 + \sigma_B^2 = 0.25;\quad \sigma_C = 0.5$

$\therefore C = 7.0 \pm 0.5$

(iii) C = 2 × 4.0 = 8.0 $\quad \sigma_C = 2 \times \sigma_A = 0.8$

$\therefore C = 8.0 \pm 0.8$

3. (i) C = 1.0 × 2.0 = 2.0

$$\left(\frac{\sigma_C}{C}\right)^2 = \left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2 = 0.25 \quad \therefore \left(\frac{\sigma_C}{C}\right) = 0.5; \quad \sigma_C = 1.0$$

$\therefore C = 2.\pm 1.$

(ii) C = 2.0/1.0 = 2.0;

As above, $\sigma_C = 1.0$, so $C = 2.\pm 1.$

Practice Exercise 11 – Answers

Find the values of x and y in the following

$y = 3x + 1$

$y = 2x + 3$

$x = \frac{3-1}{3-2} = 2$

$y = 3\times 2 + 1 = 7$ (or $2\times 2 + 3 = 7$)

$y = 3x - 1$

$y = 2x + 3$

$x = \frac{3--1}{3-2} = 4$

$y = 3\times 4 - 1 = 11$ (or $2\times 4 + 3 = 11$)

$3y = 9x + 12$

$y = 2x - 3$

$y = 3x + 4$ divide eq1 by 3

$y = 2x - 3$

$x = \frac{-3-4}{3-2} = -7$ $y = 3\times(-7) + 4 = -17$

$3y = 3x - 15$

$2y = -4x - 6$

$y = x - 5$ divide eq1 by 3

$y = -2x - 3$ divide eq2 by 2

$x = \frac{-3--5}{1--2} = \frac{2}{3}$ $y = \frac{2}{3} - 5 = -4\frac{1}{3}$

A chemical equilibrium constant, K, changes with temperature according to

$$\mathbf{RT\ ln(K) = -\Delta H^0 + T\Delta S^0} \qquad \mathbf{(R = 8.314\ J\ K^{-1}\ mol^{-1})}$$

write this in the form $\Delta H^0 = ...$

$\Delta H^0 = T\Delta S^0 - RT\ \ln(K)$ multiply by T and move ΔH^0 across

then find ΔH^0 and ΔS^0 using the experimental values

$\ln(K) = 4$ at $T = 500$ K and $\ln(K) = -4$ at $T = 1000$ K

$\Delta H^0 = 500\Delta S^0 - 8.314 \times 500 \times 4$

$\Delta H^0 = 1000\Delta S^0 - 8.314 \times 1000 \times (-4)$

$\mathbf{\Delta H^0 = 500\Delta S^0 - 16628}$

$$\mathbf{\Delta H^0 = 1000\Delta S^0 + 33256}$$

we can treat ΔH^0 as **y** and ΔS^0 as **x**

$$\Delta S^0 = \frac{33256 - -16628}{500 - 1000} = \frac{49884}{-500} = -99.77 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H^0 = -500 \times 99.77 - 16628 = 66512 \text{ J mol}^{-1}$$

Practice Exercise 12 – Answers

Solve the following quadratic expressions

$x^2 + x - 6 = 0$ **a = 1, b = 1, c = –6**

$$x = \frac{-1 \pm \sqrt{1^2 - 4\times 1\times(-6)}}{2\times 1} = \frac{-1 \pm \sqrt{25}}{2} = \frac{-1 \pm 5}{2}$$

$x = 2$ and $x = -3$ $(x - 2)(x + 3)=0$

$-2x^2 - x + 6 = 0$ **a = –2, b = –1, c = 6**

$$x = \frac{1 \pm \sqrt{(-1^2) - 4\times(-2)\times 6}}{2\times -2} = \frac{1 \pm \sqrt{49}}{-4} = \frac{1 \pm 7}{-4}$$

$x = -2$ and $x = \frac{3}{2}$ $(x + 2)(-2x + 3) =0$

$x^2 - \frac{x}{2} - \frac{1}{2} = 0$ **a = 1, b =** $-\mathbf{\frac{1}{2}}$**, c =** $-\mathbf{\frac{1}{2}}$ –or multiply by 2

$2x^2 - x - 1 = 0$ **a = 2, b = –1, c = –1**

$$x = \frac{1 \pm \sqrt{(-1)^2 - 4\times 2\times(-1)}}{2\times 2} = \frac{1 \pm \sqrt{9}}{4} = \frac{1 \pm 3}{4}$$

$x = 1$ and $x = -\frac{1}{2}$ $(x - 1)(x + \frac{1}{2}) =0$

$x + \frac{4}{x} = -5$

$x^2 + 4 = -5x$ multiply both sides by x

$x^2 + 5x + 4 = 0$ **a = 1, b = 5, c = 4**

$$x = \frac{-5 \pm \sqrt{5^2 - 4\times 4}}{2} = \frac{-5 \pm \sqrt{9}}{2} = \frac{-5 \pm 3}{2}$$

$x = -4$ $x = -1$ $(x + 4)(x +1)=0$

In overtone vibrational spectroscopy of HCl the energy of a transition, ΔE, is given by

ΔE/ (cm^{-1}) = 2991v – 53v(v+1)

where **v** is a small integer (0–5). **v** is also known as the quantum number.
If a particular transition has an energy of 8347 cm^{-1} what is the quantum number **v**?

8347 = 2991**v** -53**v**$^{\mathbf{2}}$ -53**v**

53**v**$^{\mathbf{2}}$ - 2938**v** + 8347 = 0 **a = 53, b = –2938, c = 8347**

$$\mathbf{v} = \frac{2938 \pm \sqrt{(-2938)^2 4 \times 53 \times 8337}}{2 \times 53} = \frac{2938 \pm \sqrt{6864400}}{106} = \frac{2938 \pm 2620}{106}$$

v = 3 or **v** = 52.43 - obviously **<u>v = 3</u>** is the correct physical answer.

Practice Exercise 13 – Answers

Express the following in their full form

(a) 2.998×10^8	299,800,000
(b) 3.4462×10^4	34462
(c) 123×10^5	12,300,000
(d) 1.7×10^{-5}	0.000017

Express the following in powers of 10 (one figure before the decimal point)

(a) 101325	1.01325×10^5
(b) 0.0000024	2.4×10^{-6}
(c) 255×10^4	2.55×10^6
(d) 255×10^{-9}	2.55×10^{-7}

What is the value of the following expressions ?

(a) $2^3 \times 2^4$	$2^{3+4} = 2^7 = 128$
(b) $3^{-3} \times 3^{-1}$	$3^{-3-1} = 3^{-4} = \dfrac{1}{3^4} = 0.0123$
(c) $\dfrac{\pi^3}{\pi^2 \times \pi}$	$\pi^{3-2-1} = \pi^0 = 1$
(d) $x^3 \times \dfrac{1}{x^2}$	$x^{3-2} = x^1 = x$
(e) $4^{3/2}$	$\left(\sqrt{4}\right)^3 = 2^3 = 8$
(f) $8^{-2/3}$	$\dfrac{1}{(\sqrt[3]{8})^2} = \dfrac{1}{2^2} = \dfrac{1}{4}$
(g) $\dfrac{y^{1/2}}{y^{3/2}}$	$y^{1/2-3/2} = y^{-1} = \dfrac{1}{y}$
(h) $\dfrac{x^{3/2}}{x^{0.75} \times x^{0.75}}$	$\dfrac{x^{3/2}}{x^{3/4} \times x^{3/4}} = \dfrac{x^{3/2}}{x^{3/2}} = 1$

Expand

(a) $(x^2)^5$	(b) $(x^2)^{5/2}$	(c) $\dfrac{\sqrt{\pi 3}}{\sqrt{\pi}}$	(d) $x^{2/3} \times \dfrac{1}{\sqrt{x}}$
x^{10}	$x^{2 \times 5/2} = x^5$	$\pi^{3/2-1/2} = \pi$	$x^{2/3-1/2} = x^{4/6-3/6} = x^{1/6}$

Simplify

(a) $(x^2 + 2x + 1)^{1/2} = \sqrt{(x+1)^2} = (x + 1)$ (b) $\dfrac{\sqrt{x^2 - 2x + 1}}{x^2 - 1} = \dfrac{\sqrt{(x-1)^2}}{(x-1)(x+1)} = \dfrac{1}{x+1}$

Practice Exercise 14 – Answers

Evaluate

(a) e^3 **(b)** e^{-3} **(c)** e^3e^{-3} **(d)** $\frac{1}{e^{-3}}$

20.084 $\frac{1}{e^3} = 0.0497$ $e^{3-3} = e^0 = 1$ $e^3 = 20.084$

Simplify

(a) $\frac{e^{3x}}{e^{6x}} = e^{3x-6x} = e^{-3x}$ **(b)** $\left(e^{-3y}\right)^2 = e^{-3y\times 2} = e^{-6y}$

(c) $e^{x^2}\ e^{-2x+1}$ **(d)** $\frac{e}{e^{(x+1)}}$

$e^{x^2-2x+1} = e^{(x-1)^2} = (e^{(x-1)})^2$ $e^{1-(x+1)} = e^{1-x-1} = e^{-x}$ or $\frac{1}{e^x}$

An approximation to e^x when x is small is: $e^x \approx 1 + x + \frac{x^2}{2}$

Fill in the following table (to 4 decimal places)

x	$1 + x$	$1 + x + \frac{x^2}{2}$	e^x
0.5	1.5000	1.6250	1.6487
0.3	1.3000	1.3450	1.3498
0.1	1.1000	1.1050	1.1052
0.05	1.0500	1.0513	1.0513

$$\% \text{ error} = \frac{\text{true value - approx value}}{\text{true value}} \times 100 = \frac{1.3498 - 1.3540}{1.3498} \times 100$$

$\%$ error $= -0.31\%$

Practice Exercise 15 – Answers

Evaluate **without** a calculator

(a) $\ln(e^4)$

$4\ln(e) = 4$

(b) $\ln(e^{-2}) + \log_{10}(10^3)$

$-2\ln(e) + 3\log_{10}(10) = -2 + 3 = 1$

(c) $\ln\left(\frac{1}{e^{-3}}\right) + 10^{\log_{10}(1/4)}$

$\ln(1) - \ln(e^{-3}) + \frac{1}{4}$

$0 - (-3) + \frac{1}{4} = 3.\frac{1}{4}$

Simplify

(a) $\ln\left(\frac{x}{y^3}\right)$

$\ln(x) - 3\ln(y)$

(b) $\ln\left(\frac{a}{b^2}\right)^{3/2}$

$\ln(a)^{3/2} - \ln(b^2)^{3/2}$

$= \frac{3}{2}\ln(a) - 3\ln(b)$

(c) $\ln\left(\frac{e}{e^{(x+1)}}\right)$

$\ln(e) - (x+1)\ln(e) = 1 - x - 1$

$= -x$

Express the following in terms of ln(3) and ln(2) (do not use a calculator)

(a) $\ln(6)$

$\ln(6) = \ln(2 \times 3)$
$= \ln(2) + \ln(3)$

(b) $\ln\left(\frac{1}{3}\right)$

$\ln(3^{-1}) = -\ln(3)$

(c) $\ln(8)$

$\ln(2^3) = 3\ln(2)$

(d) $\ln\left(\frac{3}{8}\right)$

$\ln(3) - \ln(8)$
$= \ln(3) + 3\ln(2)$

What is the pH of 0.8 M HCl ? What would the pH be if it only 35% dissociated?

Strong acid so $[H^+] = 0.8$ M. $\quad$ $pH = -\log_{10}[0.8] = 0.097$

35% dissociation $\quad$ $[H^+] = \frac{35}{100}\ 0.8\text{ M} = 0.28\text{ M};$ $\quad$ $pH = -\log[0.28] = 0.553$

What is the [H⁺] of a solution with a pH = 7, and one with pH = – 0.4?

$-\log_{10}\{[H^+]/M\} = 7$ $\quad$ $\log_{10}\{[H^+]/M\} = -7;$ $\quad$ $[H^+] = 10^{-7}\text{ mol dm}^{-3}$

$-\log_{10}\{[H^+]/M\} = -0.4$ $\quad$ $\log_{10}\{[H^+]/M\} = 0.4$ $\quad$ $[H^+] = 10^{0.4} = 2.51\text{ mol dm}^{-3}$

Practice Exercise 16 – Answers

1 Calculate, ν, the frequency of light required to ionise a hydrogen atom.

$$\nu = \frac{m\, e^4}{8\, \varepsilon_o^2\, h^3}$$

$m = 9.109 \times 10^{-31}$kg, $e = 1.602 \times 10^{-19}$ C,
$\varepsilon_o = 8.854 \times 10^{-12}\ J^{-1}\ C^2\ m^{-1}$, $h = 6.626 \times 10^{-34}$ J s

Many calculators cannot do this directly because me^4 is of the order 10^{-108} and $\varepsilon_o^2\ h^2$ is around 10^{-125} and give zero. We can either calculate the powers of 10 ourselves or split the calculation up such a way that we don't meet the problem

$$\nu = \frac{1}{8}\left(\frac{m}{\varepsilon_o}\right)\left(\frac{e}{\varepsilon_o}\right)\left(\frac{e}{h}\right)^3 = \frac{1}{8}\left(\frac{9.109\times10^{-31}}{8.854\times10^{-12}}\right)\left(\frac{1.602\times10^{-19}}{8.854\times10^{-12}}\right)\left(\frac{1.602\times10^{-19}}{6.626\times10^{-34}}\right)^3$$

$$= \frac{1}{8}\ 1.0288 \times 10^{-19} \times 1.8093 \times 10^{-8} \times \left(2.4177\times10^{14}\right)^3$$

$$= 0.125 \times 1.0288\times10^{-19} \times 1.8093\times10^{-8} \times 1.4133\times10^{43} = 3.288 \times 10^{15}\ \text{Hz}$$

2 The Gibbs energy ΔG^o is related to the equilibrium constant, K, by

$\Delta G^o = -RT\ \ln(K)$ find an expression for K.

$$\ln(K) = -\frac{\Delta G^o}{RT} \qquad \text{so} \qquad K = \exp\left(-\frac{\Delta G^o}{RT}\right)$$

3 The Beer-Lambert law for light absorption when light passes through a sample is

$$I_t = I_o\ 10^{-\varepsilon CL}$$

I_t is the transmitted light intensity,
I_o is the incident intensity,
ε is the extinction coefficient, and L the path length

Find an expression for the concentration C.

$$\frac{I_t}{I_o} = 10^{-\varepsilon CL} \quad \text{so} \quad \log\left(\frac{I_t}{I_o}\right) = -\varepsilon CL$$

Move I_o over and take logs (base 10) of both sides

$$C = -\frac{\log\left(\frac{I_t}{I_o}\right)}{\varepsilon L}$$

divide by εL

4 Kohlrauch's law of the conductivity of a salt is

$$\Lambda_m = \Lambda_m^0 - K\sqrt{c}$$

Λ_m is the molar conductivity,
Λ_m^0 is the molar conductivity at infinite dilution,
K is a constant

Find an expression for the concentration c. $K\sqrt{c} = \Lambda_m^0 - \Lambda_m$ so $\sqrt{c} = \dfrac{\Lambda_m^0 - \Lambda_m}{K}$; $c = \left(\dfrac{\Lambda_m^0 - \Lambda_m}{K}\right)^2$

5 A first order reaction $A \Longrightarrow X$ follows the integrated rate law

$$\ln\left(\frac{[A_o]}{[A_o] - [X]}\right) = kt$$

where $[A_o]$ is the initial concentration of A.

Find an expression for the product concentration, [X].

$$\frac{[A_o]}{[A_o] - [X]} = e^{kt}$$ exponentials of both sides

$$\frac{[A_o]}{e^{kt}} = [A_o] - [X]$$ move e^{kt} and $[A_o] - [X]$ over

$$[A_o]e^{-kt} = [A_o] - [X]$$ e^{kt} to top

$$[X] = [A_o] - [A_o]e^{-kt}$$ isolate [X]

$$[X] = [A_o](1 - e^{-kt})$$ collect common terms

6 The wavelengths λ of the Balmer series of lines in the emission spectrum of Hydrogen obey the formula

$$\frac{1}{\lambda} = R_H\left(\frac{1}{4} - \frac{1}{n^2}\right)$$ where n = 3, 4, 5, ...

find an expression for n

expand bracket

$$\frac{1}{\lambda} = \frac{R_H}{4} - \frac{R_H}{n^2}$$

move term in n^2 over and put RHS over common factor

$$\frac{R_H}{n^2} = \frac{R_H}{4} - \frac{1}{\lambda} = \frac{\lambda R_H - 4}{4\lambda}$$

invert both sides

$$\frac{n^2}{R_H} = \frac{4\lambda}{\lambda R_H - 4}$$

move R_H up and square root

$$n = \sqrt{\frac{4\lambda R_H}{\lambda R_H - 4}}$$

7 The rotational energy levels, E_n, for a diatomic molecule are given by

$E_n = B.n(n+1)$ n is the quantum number n = 0, 1, 2, 3...
.and B is a constant

Derive a formula for a transition, ΔE, between two levels with n = J+1 and n = J.

i.e. $\Delta E = E_{J+1} - E_J$.

$\Delta E = E_{J+1} - E_J = B(J+1)(J+1+1) - BJ(J+1) = B(J+1)(J+2) - BJ(J+1)$

$= B\{J^2 + 3J + 2 - J^2 - J\} = B\{2J + 2\} = 2B(J+1)$

Practice Exercise 17 – Answers

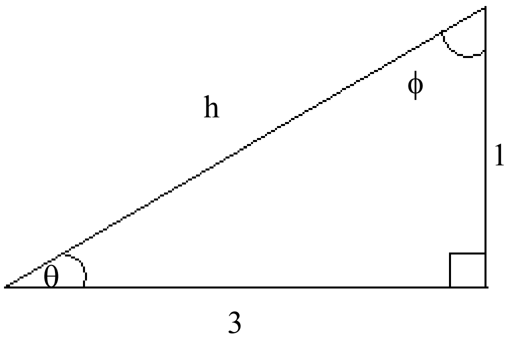
6 $45° = ?$ radians

$$45° = \frac{2\pi \times 45}{360} = \frac{2\pi \times 1}{8} = \frac{2\pi}{8} = \frac{\pi}{4}$$

7 $\frac{11}{6}\pi$ radians = ? degrees

$$\frac{11}{6}\pi \text{ radians} = \frac{360 \times \frac{11}{6}\pi}{2\pi} = \frac{360 \times \frac{11}{6}}{2} = 330°$$

8



Calculate h, cosθ, and tan ϕ. Do not evaluate the square root.

$$h = \sqrt{x^2 + y^2} = \sqrt{3^2 + 1^2} = \sqrt{10}$$

$$\cos\theta = \frac{A}{H} = \frac{3}{\sqrt{10}}$$

$$\tan\phi = \frac{O}{A} = \frac{3}{1} = 3$$

9 For what values of θ is $\cos\theta = 1$?

$\theta = 0, \pm\pi, \pm 2\pi, ...$

10 In degrees, calculate arc sin (-0.4), arc cos (0.8)

arc sin (–0.14) = –23.6°

arc cos (0.8) = 36.9°

Practice Exercise 18 – Answers

2 Calculate $\frac{dy}{dx}$ in the following cases:

m) $y = e^x$

$\frac{dy}{dx} = \mathbf{e^x}$

n) $y = \ln x$

$\mathbf{\frac{dy}{dx} = \frac{1}{x}}$

o) $y = \cos 7x$

This is of the form $y = \cos ax$ with $a = 7$

$\frac{dy}{dx} = -a \sin ax$

$\mathbf{= -7 \sin 7x}$

p) $y = 2e^{-4x} + 3 \sin x$

$$\begin{aligned}\frac{dy}{dx} &= 2\frac{d(e^{-4x})}{dx} + 3\frac{d(\sin x)}{dx}\\ &= 2 \times (-4e^{-4x}) + 3\cos x\\ &= \mathbf{-8e^{-4x} + 3\cos x}\end{aligned}$$

q) $y = \frac{2}{x} + \frac{3}{x^6}$

$y = 2x^{-1} + 3x^{-6}$

$\therefore \frac{dy}{dx} = -2x^{-2} - 18x^{-7}$

$$= -\frac{\mathbf{2}}{\mathbf{x^2}} - \frac{\mathbf{18}}{\mathbf{x^7}}$$

r) $y = 7 + 8\sqrt{x} + \dfrac{9}{\sqrt{x}}$

$$y = 7 + 8x^{1/2} + 9x^{-1/2}$$

$$\therefore \frac{dy}{dx} = 4x^{-1/2} - \frac{9}{2}x^{-3/2}$$

$$= \frac{\mathbf{4}}{\sqrt{\mathbf{x}}} - \frac{\mathbf{9}}{\mathbf{2x^{3/2}}}$$

s) $y = 2x^5 + \dfrac{3}{x^3} + 8$

$$y = 2x^5 + 3x^{-3} + 8$$

$$\therefore \frac{dy}{dx} = 10x^4 - 9x^{-4}$$

$$= \mathbf{10x^4} - \frac{\mathbf{9}}{\mathbf{x^4}}$$

t) $y = \ln(x^3) + 2x^{1/3} + \dfrac{2}{x^{1/3}}$

$$y = 3\ln x + 2x^{1/3} + 2x^{-1/3}$$

$$\therefore \frac{dy}{dx} = \frac{3}{x} + \frac{2}{3}x^{-2/3} - \frac{2}{3}x^{-4/3}$$

u) $y = 4e^{5x} + 2\sin 6x$

$$\frac{\mathbf{dy}}{\mathbf{dx}} = \mathbf{20e^{5x} + 12\cos 6x}$$

j) $y = \sin 2x \cos 3x$

here we use the Product Rule as we have the product of two functions.

i.e

$$y = uv$$

$$\frac{dy}{dx} = u\frac{dv}{dx} = v\frac{du}{dx}$$

u = sin2x and v = cos3x

therefore

$$\frac{dy}{dx} = u\frac{dv}{dx} + v\frac{du}{dx}$$

$$= -\sin 2x 3 \sin 3x + \cos 3x 2 \cos 2x$$

k) $y = 3x^2 \ln x$

Again we have a product of two functions so we use the Product Rule.
Let $u=3x^2$ and $v = \ln x$

$$\frac{dy}{dx} = u\frac{dv}{dx} + v\frac{du}{dx}$$

$$= \frac{3x^2}{x} + \ln x 6x$$

l) $y = \ln x^3$

Here we have a function of a function so we use the Chain Rule.

Let $u = x^3$

$y = \ln (u)$

$$\frac{dy}{dx} = \frac{dy}{du} \times \frac{du}{dx}$$

$$= \frac{1}{u} \times 3x^2$$

substituting

$$= \frac{1}{x^3} \times 3x^2 = \frac{3}{x}$$

2 Calculate the velocity ($v = \frac{dx}{dt}$) in the following:

a) $x = 5e^{2t} + 2t^4$

$$\mathbf{\frac{dx}{dt} = 10e^{2t} + 8t^3}$$

b) $x = 2 \cos 3t + 3 \sin 5t$

$$\frac{dx}{dt} = 2 \times -3 \sin 3t + 3 \times 5 \cos 5t$$

$$\mathbf{= -6 \sin 3t + 15 \cos 5t}$$

c) $x = \ln(t^5)$ (Hint: What do you know about $\ln x^n$?)

$$\mathbf{y = 5 \ln t}$$

$$\mathbf{\therefore \frac{dx}{dt} = \frac{5}{t}}$$

Practice Exercise 19– Answers

2 Find the stationary (turning) points of

$y = x^3 - 27x$

and give the values of y at these points.

Calculate $\frac{d^2y}{dx^2}$ and thus find whether the turning points are maxima or minima.

$\frac{dy}{dx} = 3x^2 - 27$

At a stationary point, $\frac{dy}{dx} = 0$

$\therefore 3x^2 - 27 = 0$

$x^2 = 9$

$x = +3$ or $x = -3$

$x = 3, y = 3^3 - 27 \times 3 = -54$
$x = -3, y = (-3)^3 - 27 \times (-3) = +54$

Thus there are two turning points. To determine their character we need to find $\frac{d^2y}{dx^2}$ at these points.

$\frac{d^2y}{dx^2} = \frac{d(3x^2 - 27)}{dx} = 6x$

At: x = 3; $\frac{d^2y}{dx^2} = 6 \times 3 = 18 > 0 \therefore x = 3$ is a <u>minimum</u>

At: x = –3; $\frac{d^2y}{dx^2} = 6 \times (-3) = -18 < 0 \therefore x = -3$ is a <u>maximum</u>

3 Calculate $\left(\frac{\partial f}{\partial x}\right)_y$ and $\left(\frac{\partial f}{\partial y}\right)_x$ in the following cases:

a) $f(x,y) = x^3 + 2y^4 + x^2y^2$
b) $f(x,y) = x\sin y + y\cos x + 3xy$

a) $\left(\frac{\partial f}{\partial x}\right)_y = 3x^2 + 2xy^2$; $\left(\frac{\partial f}{\partial y}\right)_x = 8y^3 + 2x^2y$

b) $\left(\frac{\partial f}{\partial x}\right)_y = \sin y - y\sin x + 3y$; $\left(\frac{\partial f}{\partial y}\right)_x = x\cos y + \cos x + 3x$

3. Integrate the following f(x):

a) $f(x) = \frac{3}{x^2}$

$f(x) = 3x^{-2}$

$\int f(x)dx = 3 \times \frac{x^{-1}}{-1} + c$

$\mathbf{= -\frac{3}{x} + c}$

b) $f(x) = \frac{2}{\sqrt{x}}$

$f(x) = 2x^{-1/2}$

$\int f(x)dx = 2 \times \frac{x^{1/2}}{1/2} + c$

$\mathbf{= 4x^{1/2} + c}$

c) $f(x) = 1 + 3x^2$

$\int f(x)dx = x + 3 \times \frac{x^3}{3} + c$

$$= \mathbf{x + x^3 + c}$$

d) $f(x) = 2e^{-x} + 3e^{-2x}$

$$\int f(x)dx = 2\times(-e^{-x}) + 3\times\left(-\frac{1}{2}e^{-2x}\right) + c$$

$$= \mathbf{-2e^{-x} - \frac{3}{2}e^{-2x} + c}$$

4. Calculate x in the following cases:

c) $\frac{dx}{dt} = \frac{2}{t}$; $\quad$ x = 2 when t = 1

$$x = \int \frac{2}{t}dt = 2\ln t + c$$

Substitute x=2 and t=1 to find c, i.e.

$2 = 2\ln 1 + c$ $\qquad$ c = 2

$$\therefore \mathbf{x = 2\ln t + 2}$$

d) $\frac{dx}{dt} = 3 + 5t^3$; x = 0 when t = 0

$$x = \int \left(3 + 5t^3\right)dt = 3t + \frac{5}{4}t^4 + c$$

Substitute x = 0 and t = 0 to find c, i.e.

$$0 = 0 + c$$
$$c = 0$$

$$\therefore \mathbf{x = 3t + \frac{5}{4}t^4}$$

5. In second order kinetics $\frac{d[A]}{dt} = -k_2[A]^2$

If [A] = $[A]_0$ at t = 0, show:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t$$

$$\int \frac{d[A]}{[A^2]} = -k_2 \int dt = -k_2 t$$

$$\therefore -\frac{1}{[A]} = -k_2 t + c$$

$$t = 0,\ [A] = [A]_0 \quad ; -\frac{1}{[A]_0} = c$$

$$\therefore -\frac{1}{[A]} = -k_2 t - \frac{1}{[A]_0} \quad \text{(times } -1\text{)}$$

$$\frac{1}{[A]} = k_2 t + \frac{1}{[A]_0}$$

Practice Exercise 20 – Answers

4 Calculate $\int f(x)dx$ in the following cases:

c) $f(x) = 6 + 2\sqrt{x} + \frac{3}{x^5}$

$f(x) = 6 + 2x^{1/2} + 3x^{-5}$

$\int f(x)dx = 6x + \frac{2x^{3/2}}{3/2} - \frac{3x^{-4}}{4} + c$

$\mathbf{= 6x + \frac{4}{3}x^{3/2} - \frac{3}{4x^4} + c}$

d) $f(x) = 2\cos(2x) + 3e^{3x} + 4x^{3/2}$

$\int f(x)dx = 2 \times \frac{1}{2}\sin 2x + 3 \times \frac{1}{3}e^{3x} + 4 \times \frac{x^{5/2}}{5/2} + c$

$\mathbf{= \sin 2x + e^{3x} + \frac{8}{5}x^{5/2} + c}$

5 Calculate x in the following cases:

a) $\frac{dx}{dt} = \frac{3}{t} + 2t$; x = 1 when t = 1

$x = 3\ln t + t^2 + c$

Set x = 1 and t = 1 to determine c

$1 = 3\ln 1 + 1^2 + c$ c = 0

$\therefore \mathbf{x = 3\ln t + t^2}$

b) $\frac{dx}{dt} = 2e^{-5t}$; x = 1 when t = 1

$$x = 2 \times \left(\frac{1}{-5} e^{-5t} \right) + c$$

$$= -\frac{2}{5} e^{-5t} + c$$

Set x = 1 and t = 1 to determine c.

$$1 = -\frac{2}{5} e^{-5} + c$$

$$\therefore c = 1 + \frac{2}{5} e^{-5}$$

$$\therefore \mathbf{x = 1 + \frac{2}{5} e^{-5} - \frac{2}{5} e^{-5t}}$$

6 Calculate the following definite integrals:

a) $\int_{-1}^{1} \left[x^3 + x^5 \right] dx$

$$= \left[\frac{x^4}{4} + \frac{x^6}{6} + c \right]_{-1}^{1}$$

$$= \left\{ \frac{1^4}{4} + \frac{1^6}{6} + c \right\} - \left\{ \frac{(-1)^4}{4} + \frac{(-1)^6}{6} + c \right\}$$

$$= \frac{5}{12} - \frac{5}{12}$$

$$= \mathbf{0}$$

(b)

$$\int_{1}^{2} \left(e^{2t} + \frac{3}{t^2} \right) dt = \left[\frac{e^{2t}}{2} - \frac{3}{t} \right]_{1}^{2}$$

$$= \left\{ \frac{e^4}{2} - \frac{3}{2} + c \right\} - \left\{ \frac{e^2}{2} - \frac{3}{1} + c \right\}$$

$$= \mathbf{\frac{e^4}{2} - \frac{e^2}{2} + \frac{3}{2}}$$