

Appendix 1: Mathematical background (AS and A Level)

Exponents

A simple expression such as $X \times Y$ means that the two numbers are to be multiplied together. An **exponent** has the form X^Y . This means that X is to be multiplied by itself Y times. For example $3^4 = 3 \times 3 \times 3 \times 3 = 81$. The exponents of 10 are easy to understand: $10^1 = 10$, $10^2 = 100$, $10^3 = 1000$. Each term in the series is 10 times as

large as the previous one. What about 10^0 ? Because $10^1 = 10$, 10^0 must equal $\frac{10^1}{10} = 1$. In general $X^0 = 1$ and this is true for any value of X. If we now consider 10^{-1} , we are dividing 10^0 (which is equal to 1) by 10. So

10^{-1} must equal $\frac{1}{10}$. In general $10^{-Y} = \frac{1}{10^Y}$. In chemistry, we quite often come across numbers with negative exponents. These can be very small numbers indeed; for example 10^{-12} is one divided by a million million. A summary of some exponent values of 2 is given in Table A1.1.

Table A1.1 Some values of exponents of 2

Exponents	2^{-6}	2^{-4}	2^{-2}	2^0	2^2	2^4	2^6
Numerical value	$\frac{1}{64}$	$\frac{1}{16}$	$\frac{1}{4}$	1	4	16	64

Significant figures

Relative atomic masses are given to one place of decimals. For common elements, such as carbon and oxygen, this corresponds to an accuracy of about 1%. Titration results are usually 0.1 cm^3 in 25 cm^3 , which corresponds to an accuracy of 0.4%. This means that we are not justified in giving answers with an accuracy much greater than 1%. A calculator often gives eight figures in the answer. It would be quite wrong to give all these figures in your answer, which implies that the error is very much less than 1%. The sensible number of figures to give is three which indicates an error of about 1%; two figures are too few (it may indicate an error of 10%) and four figures are too many (it indicates an error less than 0.1%). We use the phrase '*to three significant figures*' after we have adjusted the value from the calculator. If the fourth figure is <5 , we take the first three figures; if the fourth figure is ≥ 5 , we add one to the third figure.

Examples

Give the following numbers to three significant figures.

- a) 1782
- b) 3.6518002
- c) 0.0065489002
- d) 3.56503×10^7

Answers

- a) 1780
- b) 3.65
- c) 0.00655
- d) 3.57×10^7

When quoting a corrected answer, write: '**Answer 3.57×10^7 to three sig. figs**'.

Precision, error and accuracy

Precision

A balance may have a **precision** of 0.01 g. This means that, for example, a reading of 34.68 g has a value of 34.68 ± 0.005 g. This variation is also termed **random error** or **experimental error**. Precise readings are said to be **repeatable**; if they are repeatable when the apparatus is used by other people at different times, they are said to be **reproducible**.

Error

If the balance is incorrectly zeroed, all readings may be too high or too low. This is called **systematic error** and is eliminated by subtraction weighing. The sum of systematic error and random error is called the **absolute error**. Error divided by the true value is the **relative error**, often expressed as a percentage.

Accuracy

A reading that has a small error is said to be **accurate**.

Rearranging formulae

A formula is often of the form $a = b/c$ and we may need to rearrange the formula so that it shows the value, not for a , but for b or c . An example is the formula $n = m/M$, where n is number of moles, m is mass and M is molar mass. If we need to make either m or M the subject, we first multiply both sides of the expression by the denominator, M . We then have

$$nM = m$$

This gives us an expression for m .

To give us an expression for M , we need to divide both sides of the expression by n , which becomes

$$M = m/n$$

Check that the units are correct. M , the molar mass, has units g mol^{-1} ; m , the mass, has units g ; n , number of moles, has units mol . The units of the left-hand side are g mol^{-1} and the units on the right-hand side are g/mol which is also g mol^{-1} .

A very common example of a formula that often needs rearranging is the titration equation $n = c \times v/1000$. To express it in either c or v , we first multiply by 1000. We have then

$$1000n = c \times v$$

To obtain the expressions for c or v , we divide by either v or c . We then have

$$v = 1000n/c \text{ and } c = 1000n/v$$

The units of c are mol dm^{-3} , the units of n are mol and the units of v are cm^3 . The units on the left-hand side of the first expression are cm^3 and the right-hand side are $1000 \times \text{mol}/(\text{mol dm}^{-3})$, which also equals cm^3 as $1000 \text{ cm}^3 = 1 \text{ dm}^3$.

Worked examples

- a) Using a solution of concentration $0.0971 \text{ mol dm}^{-3}$, the end-point of a titration was 26.1 cm^3 . How many moles is this?
- b) What is the concentration of a solution in which 0.0357 mol of a substance was made up 250 cm^3 ?
- c) What volume of a $0.0865 \text{ mol dm}^{-3}$ solution of NaOH is need to neutralise $3.05 \times 10^{-3} \text{ mol}$ of sulfuric acid?

Answers

- a) $0.0971 \times 26.1/1000 = 2.53 \times 10^{-3} \text{ mol}$
- b) $1000 \times 0.0357/250 = 0.143 \text{ mol dm}^{-3}$
- c) As sulfuric acid is dibasic, one mole is neutralised by two moles of NaOH . Moles of NaOH needed is $3.05 \times 10^{-3} \times 2 = 6.10 \times 10^{-3} \text{ mol}$. Volume needed $= 1000 \times 3.05 \times 10^{-3}/0.0865 = 35.3 \text{ cm}^3$

Units

Most numerical answers have **units** (that means they are not just numbers). Some common units are grammes per cubic centimetre and moles per cubic decimetre. These are written as g cm^{-3} and mol dm^{-3} not g/cm^3 and mol/dm^3 . This is because the solidus (/) has a special use for labelling graphs (see below). The explanation of exponents given on page 1 shows us that $\text{cm}^{-3} = 1/\text{cm}^3$ and $\text{dm}^{-3} = 1/\text{dm}^3$.

Numerical answers are often written in **standard form**; that is, in the form $a.bc \times 10^d$. An example of this is an answer to one of the questions we met earlier, 3.57×10^7 . To avoid having large or small values of exponents, we use the prefixes given in Table A1.2.:

Table A1.2 Some common prefixes

Name	pico	nano	micro	milli	kilo	mega
Symbol	p	n	μ	m	k	M
Value	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^3	10^6

Because there are different prefixes, there are at least two ways of expressing an answer. An example of this is the wavelength of sodium light; this can be given either as 590 nm or 0.590 μm . The common usage is 590 nm. Another example is the ionic radius of sodium which can be given either as 0.102 nm or 102 pm. In this case, the common usage is 0.102 nm.

Strict SI usage allows changes only by factors of 10^3 .

Exceptions to this rule are the use of cm^3 and dm^3 ; these are so common that they are used instead of the unfamiliar μm^3 and mm^3 . (Centi, c, is 10^{-2} and deci, d, is 10^{-1} .)

Drawing graphs

When drawing graphs, it is important to use a sensible scale. A typical piece of A4 **graph** paper has 9×14 large squares. Look at the largest values to be plotted on the two axes and select an appropriate scale. For example, if the largest values are 175 and 60, use 9 and 6 large squares; the 9 will be labelled to 180 (20 units per large square) and the 6 labelled to 60 (10 units per large square). A large square is easily divided into 2, 5 or 10; avoid divisions into 3 or 4 which are difficult to cope with.

Draw in the two axes in ink and put in the main divisions with a short line and a number. If the origin is included, put in '0' on both axes.

Label the axes with what is being plotted. Use a solidus (/) followed by units; for example *time/s* or *concentration/mol dm⁻³*. This removes the units so that the points you are plotting on the graph are pure numbers.

One variable is **independent** of the experiment being performed. In chemistry this is often time or volume added which is plotted on the *x*-axis (the horizontal one). The other variable is **dependent** on the experiment being performed and is plotted on the *y*-axis (the vertical one). Likely dependent variables are temperature (for example from a cooling curve), concentration or rate (from a kinetics experiment) or pH (from a titration curve).

Put the points to be plotted in a table at the top-right-hand corner of the graph. The first column should be the dependent variable (*y*-axis), the second the independent variable (*x*-axis).

Plot the points in pencil using a small cross. (In the unlikely event of having to plot two graphs on the same sheet of paper, use small circles to indicate the second set of points.) Decide whether you have to include the origin. By inspection, determine whether the points lie on a straight line or a curve. If the points lie on a straight line, use a ruler for the best fit; for a curve you will probably have to draw freehand. If the origin is included, the line must pass through it.

You may be asked to obtain data from the graph. Some likely examples are given below.

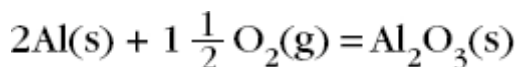
- 1 Read off a flat portion (e.g. a cooling curve).
- 2 Work out a gradient (e.g. from a concentration against time graph in kinetics to obtain the rate). This is easy if the graph is a straight line; it is much harder if it is a curve as you will have to draw a tangent to the graph at the point selected. This is very difficult to get right and the result will be very unreliable.
- 3 Read off the value of an intermediate point (**interpolation**, which is reliable) or of a point found by extending the graph (**extrapolation**, which is unreliable).

Be careful not to give the result to an unjustified degree of accuracy.

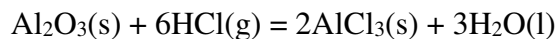
Distinguish between a graph and a diagram. The plot of melting point of elements against proton number ([Figure 10.5](#)) is not a graph. The points may be joined up to show a general trend but they do not lie on a line of best fit.

The Δ notation

A 'Δ' (Greek letter delta) indicates a change. For example ΔH_f is the enthalpy change when a substance is formed from its elements. This is equal to the enthalpy of the substance minus the enthalpy of the elements. The enthalpy of all elements is made zero by definition. For example ΔH_f of aluminium oxide, represented by the equation



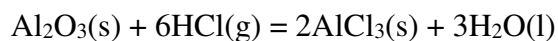
can be determined because the enthalpy of $2\text{Al(s)} + 1\frac{1}{2}\text{O}_2\text{(g)}$ is zero. If we have tables of enthalpy changes of formation, we can calculate the enthalpy change of reaction such as



In general, $\Delta H_f = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$

Often we use **standard enthalpy changes**, represented by ΔH° . These are enthalpy changes for reactions carried out under specified conditions, generally a pressure of 1 bar (or 1 atm) at a temperature of 298 K.

Another use of Δ is Δn . This is the total number of species on the right-hand side of the equation minus the total number of species on the left-hand side of the equation. For the equation

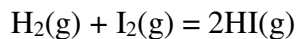


$$\Delta n = (2 + 3) - (1 + 6) = -2.$$

We shall come across Δn again when we look at K_c and K_p .

Equilibrium constants

Consider a reaction in which $\Delta n = 0$. For example



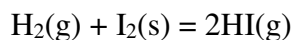
$$K_c = [\text{HI}]^2/([\text{H}_2][\text{I}_2]) \text{ and } K_p = p_{\text{HI}}^2/(p_{\text{H}_2} \times p_{\text{I}_2})$$

The units of K_c are $(\text{mol dm}^{-3})^2/(\text{mol dm}^{-3} \times \text{mol dm}^{-3}) = 0$.

Similarly, the units of K_p are $\text{atm}^2/(\text{atm} \times \text{atm}) = 0$

So for a reaction in which $\Delta n = 0$, there are no units for K_c and K_p .

If there is a change in number of molecules, Δn , K_c and K_p will have units. Consider the reaction

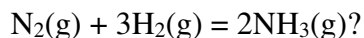


$K_c = [\text{HI}]^2/[\text{H}_2]$. We omit the $\text{I}_2\text{(s)}$ term as it is a constant.

$K_p = p_{\text{HI}}^2/p_{\text{H}_2}$. Again we omit the $\text{I}_2\text{(s)}$ term because it has a fixed partial pressure at a given temperature. As $\Delta n = +1$, there will be units for K_c (mol dm^{-3}) and K_p (atm). In general, the units of K_c will be $(\text{mol dm}^{-3})^{\Delta n}$ and the units of K_p will be $\text{atm}^{\Delta n}$.

Worked example

a) What are the units of K_c for the reaction



b) What are the units of K_p for this reaction?

Answer

$$\Delta n = -2$$

a) The units of K_c are $\text{mol}^{-2} \text{dm}^6$.

b) The units of K_p are atm^{-2} .

Logarithms (A Level only)

A **logarithm** is the reverse of an exponent. If $Y = 10^X$, $X = \log Y$. For example if $Y = 100$, $X = 2$. We then have $\log 10 = 1$, $\log 100 = 2$ and $\log 1000 = 3$. Extending the values to 0 and negative numbers, we have $\log 1 = 0$, $\log 0.1 = -1$ and $\log 0.01 = -2$. If we ask what is the value of the logarithm of a number like 200 (which is between 100 and 1000), we know that it will be >2 and <3 . We can use a calculator to find the value. We need use the log button (not the ln button) on the number 200. The answer is 2.30.

Worked example

What are the logarithms of these numbers?

a) 450

b) 2.6

c) 0.03

d) 2.4×10^{-5}

Answers

a) 2.65

b) 0.414

c) -1.52

d) -4.62

You will also need to be familiar with the reverse process; that is using a calculator to find a number given its logarithm. This is very important when calculating pH values.

Worked example

What numbers have the following logarithms?

a) 3.50

b) 0.26

c) -5.82

d) -0.56

Answers

a) 3160

b) 1.82

c) 1.51×10^{-6}

d) 0.275

The number e (A Level only)

There is a special number **e** which has a value of 2.72 to three significant figures. It originates from calculus. Sometimes exponents or logarithms are given to the base e, rather than to the base 10 which is the base we have been using. They are written as e^x (or sometimes $\exp(x)$) for exponents and $\log_e X$ or $\ln X$ for logarithms. We can work out these values using a calculator in the same way we use calculators to work out values of 10^x and $\log_{10} X$.

Worked examples

1 Use your calculator to work out

a) $e^{3.72}$

b) $e^{-1.36}$

c) $\ln 1560$

d) $\ln 0.000352$

e) 7.38×10^{-8} .

2 What is the value of $\exp(-E/RT)$ when $E = 50.0 \text{ kJ mol}^{-1}$, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ and $T = 298 \text{ K}$?

Answers

1 a) 41.3

b) 1.24×10^{-6}

c) 7.35

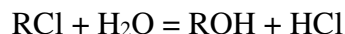
d) -7.95

e) -16.4

2 1.70×10^{-9}

Calculus notation (A Level only)

You are not expected to know any calculus but if you have done some, the mathematical treatment of kinetics will become much clearer. If we have a reaction such as the hydrolysis of an alkyl chloride



then rate is equal either to the rate of disappearance of a reactant or the rate of appearance of a product. As an approximation, we can write

$$\text{rate} = -\Delta[\text{RCl}]/t$$

which becomes exact if we make our changes increasingly small. Then

$$\text{rate} = -d[\text{RCl}]/dt = d[\text{ROH}]/dt = d[\text{HCl}]/dt$$

Note the ‘-’ sign in the first term. This arises because $[\text{RCl}]$ is decreasing and rates must always be positive.

We can see that a rate is the gradient of a concentration/time graph. That is why for approximate work, we often let

$$-d[R]/dt \approx -\Delta R/t$$

or

$$d[P]/dt \approx \Delta[P]/t$$

Usually the order of a reactant is zero, first or second. These three examples are illustrated in [Figure 21.4](#) in the textbook. A particularly important case is if a reactant is first order. We have

$$\text{rate} = -d[R]/dt = k[R]$$

Rearranging we have

$$[d[R]/[R] = k]dt$$

between the limits t and zero.

$$\ln[R] - \ln[R_0] = -kt$$

where \ln is a logarithm to the base e
and

$$[R] = [R_0]\exp(-kt)$$

(It is sometimes clearer to write $\exp(-kt)$ rather than e^{-kt} .)

A special case is if $[R] = \frac{1}{2} [R_0]$. Then $\exp(-kt_{1/2}) = 1/2$, where $t_{1/2}$ is the half-life of the reaction.
Thus

$$t_{1/2} = \ln 2/k = 0.693/k$$

This shows that the half-life is independent of the initial concentration R_0 and provides a ready means of identifying a first order reaction and for determining the value of the rate constant k .

We can often decide whether the order of a reactant is 0, 1, 2 or 3 by studying how the concentration of the reactant varies with time, as shown by [Figure 21.4](#) in the textbook.

We have just shown that for first order there is an exponential decrease. For zero order, the graph is a straight line and for second order, a graph that is steeper than exponential.

The units of k depend on what is the overall order of the reaction. The most common overall values are 1, 2 or 3.

The rate = $k[\text{reactant or product terms}]^n$ where $n = 1, 2$ or 3 .

The units of rate are $\text{mol dm}^{-3} \text{s}^{-1}$.

If $n = 1$, we have $\text{mol dm}^{-3} \text{s}^{-1} = k \text{ mol dm}^{-3}$ and the units of k are s^{-1} .

If $n = 2$, we have $\text{mol dm}^{-3} \text{s}^{-1} = k \text{ mol}^2 \text{ dm}^{-6}$ and the units of k are $\text{mol}^{-1} \text{ dm}^3 \text{s}^{-1}$.

If $n = 3$, we have $\text{mol dm}^{-3} \text{s}^{-1} = k \text{ mol}^3 \text{ dm}^{-9}$ and the units of k are $\text{mol}^{-2} \text{ dm}^6 \text{s}^{-1}$.

Further reading

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