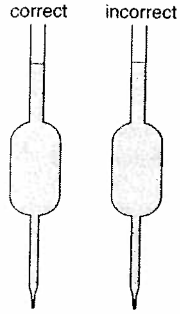
# Uncertainty and error in measurement

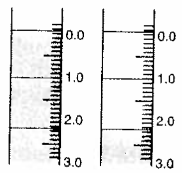
## RANDOM UNCERTAINTIES AND SYSTEMATIC ERRORS

Quantitative chemistry involves measurement. A measurement is a method by which some quantity or property of a substance is compared with a known standard. If the instrument used to take the measurements has been calibrated wrongly or if the person using it consistently misreads it then the measurements will always differ by the same amount. Such an error is known as a **systematic error**. An example might be always reading a pipette from the sides of the meniscus rather than from the middle of the meniscus.

correct incorrect



a systematic error will be introduced if a pipette is read incorrectly




systematic errors may cancel out when a difference in two readings is taken $\Delta V = 2.0\ cm^3$ whether the burette is read correctly or incorrectly.

**Random uncertainties** occur if there is an equal probability of the reading being too high or too low from one measurement to the next. These might include variations in the volume of glassware due to temperature fluctuations or the decision on exactly when an indicator changes colour during an acid base titration.

## PRECISION AND ACCURACY

**Precision** refers to how close several experimental measurements of the same quantity are to each other. **Accuracy** refers to how close the reading are to the true value. This may be the standard value, or the literature or accepted value. A measuring cylinder used to measure exactly 25 $cm^3$ is likely to be much less accurate than a pipette that has been carefully calibrated to deliver exactly that volume. It is possible to have very precise readings which are inaccurate due to a systematic error. For example all the students in the class may obtain the same or very close results in a titration but if the standard solution used in all the titrations had been prepared wrongly beforehand the results would be inaccurate due to the systematic error. Because they are always either too high or too low systematic errors cannot be reduced by repeated readings. However random errors can be reduced by repeated readings because there is an equal probability of them being high or low each time the reading is taken. When taking a measurement it is usual practice to report the reading from a scale as the smallest division or the last digit capable of precise measurement even though it is understood that the last digit has been rounded up or down so that there is a random error or uncertainty of ± 0.5 of the last unit.

## SIGNIFICANT FIGURES

Whenever a measurement of a physical quantity is taken there will be a random uncertainty in the reading. The measurement quoted should include the first figure that is uncertain. This should include zero if necessary. Thus a reading of 25.30 °C indicates that the temperature was measured with a thermometer that is accurate to + 0.01 °C. If a thermometer accurate to only ± 0.1 °C was used the temperature should be recorded as 25.3 °C.

Zeros can cause problems when determining the number of significant figures. Essentially zero only becomes significant when it comes *after* a non-zero digit (1,2,3,4,5,6,7,8,9).

| | | | |
|---|---|---|---|
| 000123.4 | 0.0001234 | 1.0234 | 1.2340 |
| zero not a significant figure | | zero is a significant figure | |
| values quoted to 4 sig. figs. | | values quoted to 5 sig. figs. | |

Zeros after a non-zero digit but before the decimal point may or may not be significant depending on how the measurement was made. For example 123 000 might mean exactly one hundred and twenty three thousand or one hundred and twenty three thousand to the nearest thousand. This problem can be neatly overcome by using scientific notation.

$1.23000 \times 10^6$ quoted to six significant figures
$1.23 \times 10^6$ quoted to three significant figures.

**Calculations**

**1.** When adding or subtracting it is the number of decimal places that is important. Thus when using a balance which measures to ± 0.01 g the answer can also be quoted to two decimal places which may increase or decrease the number of significant figures.

| | | | | | |
|---|---|---|---|---|---|
| e.g. | 7.10 g<br>3 sig. figs. | + | 3.10 g<br>3 sig. figs. | = | 10.20 g<br>4 sig. figs. |
| | 22.36 g<br>4 sig. figs. | – | 15.16 g<br>4 sig. figs. | = | 7.20 g<br>3 sig. figs. |

**2.** When multiplying or dividing it is the number of significant figures that is important. The number with the least number of significant figures used in the calculation determines how many significant figures should be used when quoting the answer.

e.g. When the temperature of 0.125 kg of water is increased by 7.2 °C

the heat required
$= 0.125\ kg \times 7.2\ °C \times 4.18\ kJ\ kg^{-1}\ °C^{-1}$
$= 3.762\ kJ.$

Since the temperature was only recorded to two significant figures the answer should strictly be given as 3.8 kJ.

# Uncertainties in calculated results and graphical techniques

## ABSOLUTE AND PERCENTAGE UNCERTAINTIES

When making a single measurement with a piece of apparatus the absolute uncertainty and the percentage uncertainty can both be stated relatively easily. For example consider measuring 25.0 $cm^3$ with a 25 $cm^3$ pipette which measures to ± 0.1 $cm^3$. The absolute uncertainty is 0.1 $cm^3$ and the percentage uncertainty is equal to:

$$\frac{0.1}{25.0} \times 100 = 0.4\%$$

If two volumes or two masses are simply added or subtracted then the absolute uncertainties are added. For example suppose two volumes of 25.0 $cm^3$ ± 0.1 $cm^3$ are added. In one extreme case the first volume could be 24.9 $cm^3$ and the second volume 24.9 $cm^3$ which would give a total volume of 48.8 $cm^3$. Alternatively the first volume might have been 25.1 $cm^3$ which when added to a second volume of 25.1 $cm^3$ gives a total volume of 50.2 $cm^3$. The final answer therefore can be quoted between 48.8 $cm^3$ and 50.2 $cm^3$, that is, 50.0 $cm^3$ ± 0.2 $cm^3$.

When using multiplication, division or powers then percentage uncertainties should be used during the calculation and then converted back into an absolute uncertainty when the final result is presented. For example, during a titration there are generally four separate pieces of apparatus, each of which contributes to the uncertainty.

e.g. when using a balance that weighs to ± 0.001 g the uncertainty in weighing 2.500 g will equal

$$\frac{0.001}{2.500} \times 100 = 0.04\%$$

Similarly a pipette measures 25.00 $cm^3$ ± 0.04 $cm^3$.

The uncertainty due to the pipette is thus

$$\frac{0.04}{25.00} \times 100 = 0.16\%$$

Assuming the uncertainty due to the burette and the volumetric flask is 0.50% and 0.10% respectively the overall uncertainty is obtained by summing all the individual uncertainties:

$$\text{Overall uncertainty} = 0.04 + 0.16 + 0.50 + 0.10 = 0.80\% \approx 1.0\%$$

Hence if the answer is 1.87 mol $dm^{-3}$ the uncertainty is 1.0% or 0.0187 mol $dm^{-3}$

The answer should be given as 1.87 ± 0.02 mol $dm^{-3}$.

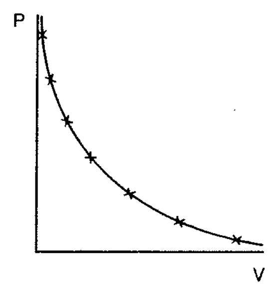
If the generally accepted 'correct' value (obtained from the data book or other literature) is known then the total error in the result is the difference between the literature value and the experimental value divided by the literature value expressed as a percentage. For example, if the 'correct' concentration for the concentration determined above is 1.90 mol $dm^{-3}$ then:

$$\text{the total error} = \frac{(1.90 - 1.87)}{1.90} \times 100 = 1.6\%.$$

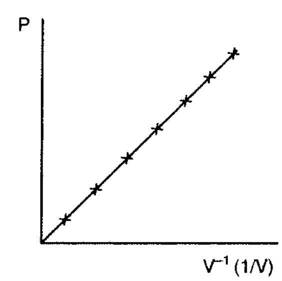
## GRAPHICAL TECHNIQUES

By plotting a suitable graph to give a straight line or some other definite relationship between the variables graphs can be used to predict unknown values. There are various methods to achieve this. They include measuring the intercept, measuring the gradient, extrapolation and interpolation. **Interpolation** involves determining an unknown value within the limits of the values already measured. **Extrapolation** (see example on page 29) requires extending the graph to determine an unknown value which lies outside the range of the values measured. If possible manipulate the data to produce a straight line graph. For example, when investigating the relationship between pressure and volume for a fixed mass of gas a plot of P against V gives a curve whereas a plot of P against 1/V will give a straight line. Once the graph is in the form of y = mx + c then the values for both the gradient (m) and the intercept (c) can be determined.

sketch graph of pressure against volume for a fixed mass of gas at a constant temperature




sketch graph of pressure against the reciprocal of volume for a fixed mass of gas at a constant temperature




The following points should be observed when drawing a graph.

- Plot the independent variable on the horizontal axis and the dependent variable on the vertical axis.
- Choose appropriate scales for the axes.
- Use Standard International (SI) units wherever possible.
- Label each axis and include the units.
- Draw the line of best fit.
- Give the graph a title.

**Measuring a gradient from a graph**