

UNCERTAINTIES AND ERRORS

A. Uncertainties in raw data

When numerical data are collected, the values cannot be determined exactly, regardless of the nature of the scale or the instrument or the care taken by the operator. If the mass of an object is determined with a digital balance reading to 0.1 g, the actual value lies in a range above and below the reading. This range is the uncertainty of the measurement. If the same object is measured on a balance reading to 0.001 g, the uncertainty is reduced, but can never be completely eliminated.

In Data Collection, estimated uncertainties should be indicated for all measurements, as stated above. These uncertainties may be estimated in different ways:

1. from the last significant figure in a measurement (as for a digital balance)
2. from the smallest division (as for a measuring cylinder)
3. from data provided by the manufacturer (printed on the apparatus or available in an instruction manual or in the manufacturer's catalogue)

For the first source above, a common procedure is to take the uncertainty as half of the last place of significant figures. Thus, for a digital balance recording to 0.001g, the uncertainty of a single reading would be + 0.0005 g. Since a mass measurement of an object is the difference between two mass readings (even if one is 0.000g), the total uncertainty is the sum of the two values, hence +0.001 g in the example above.

Where measurements are made with a continuous scale, half of the smallest division is often taken as the uncertainty. If this seems too large, then a smaller value can be used. As an example, consider a titration with a 50 cm burette, where the smallest division is 0.1 cm but students are expected to read values to 0.01 cm. A single reading has an uncertainty which surely is larger than +0.005 cm but probably smaller than +0.05 cm. A value of +0.03 or +0.02 cm would be reasonable, although +0.05 cm could also be used. The required uncertainty of a grade A burette is +0.03 cm for a single reading. The important consideration is not to produce a "correct" value, but to use a reasonable value that has been obtained by application of consistent principles.

Here is an example where a student measured temperature for the melting point of 1,4-dichlorobenzene. She wrote the following qualitative and quantitative comments:
"The temperature changed continuously with time below and above the melting point. Therefore, the values recorded have an uncertainty greater than the least significant digit of each measurement of +0.2 C. The uncertainty was estimated to be more like +0.5 C."

The combination of these estimated uncertainties of individual measurements, to obtain the uncertainty value calculated from several measurements, will be discussed under Data Processing and Presentation.

B. Uncertainties and errors in Data Processing

THE CHIEF EXAMINER FOR INTERNAL ASSESSMENT RECENTLY SENT OUT THE FOLLOWING:

Expectations at Standard Level and Higher Level

Standard level candidates are not expected to process uncertainties in calculations. However, they can make statements about the minimum uncertainty, based on the least significant figure in a measurement, and can also make statements about the manufacturer's claim of accuracy. They can estimate uncertainties in compound measurements, and can make educated guesses about uncertainties in the method of measurement. If uncertainties are small enough to be ignored, the candidate should note this fact.

Higher level candidates should be able to express uncertainties as fractions and as percentages. They should also be able to propagate uncertainties through a calculation.

Note: Standard level and higher level candidates are not expected to construct uncertainty bars on their graphs.

1. Definitions

Errors in experimental work can be divided into two types:

Random Error: A random error makes the measured value both smaller and larger than the true value. Chance alone determines if it is smaller or larger. Reading the scales of a balance, graduated cylinder, thermometer, etc produces, random errors. Note: reading the scales of measuring devices correctly, produces random errors. They cannot be avoided, they are part of the measuring process. Uncertainties are measures of random error.

Systematic Error: A systematic error makes the measured value always smaller or larger than the true value, but **not both**. An experiment may involve more than one systematic error and these errors may nullify one another but each alters the true value in one way only. Accuracy (or validity) is a measure of the systematic error. If an experiment is accurate or valid then the systematic error is very small. Accuracy is a measure of how well an experiment measures what it was trying to measure. Assuming that no heat is lost in a heat experiment is a systematic error when a Styrofoam cup is used as a calorimeter. Thus, the measured value for heat gained by the water will always be too low. When an accepted value is available for a result determined by experiment, the percent error can be calculated:

$$\frac{\text{experimental value} - \text{accepted value}}{\text{accepted value}} \times 100 = \% \text{ error}$$

Uncertainty: The uncertainties of individual measurements have been discussed above, under Data Collection. The terms “**precision**” and “reliability” are closely related to “uncertainty”. The two terms are equivalents, and are the inverse of uncertainty. Where uncertainty is relatively low, precision is relatively high. Another measure of uncertainty or precision arises when an experiment is repeated many times, yielding several results from which an average value can be calculated. The precision is a measure of how close the results are to the average value. The uncertainty (here called “**experimental uncertainty**”) is a measure of how far apart the results are from the average value. This usually is calculated either as the average (and percent average) deviation or as the standard (and percent standard) deviation compared to the average of

the final results. The average value always should be the average of the final results calculated for each trial, rather than the average of raw data or the results of intermediate calculations. This uncertainty of an experiment is a measure of the random error. If the uncertainty is low, then the random error is small.

Example 1: Standardization of NaOH by titration

The following concentrations in mol dm⁻³, were calculated from the results of three trials:
6.0987, 0.0961, 0.1020

The average value is 0.0989 and the average deviation is 0.0020

Since uncertainties are meaningful only to one significant figure, the result should be reported as follows:

Concentration = 0.099 ± 0.002 mol dm⁻³

The uncertainty, and hence the possible random error, also can be estimated from the uncertainties of individual measurements which are required for a particular determination. In a calorimetry experiment, for example, the uncertainty in the quantity of heat produced will be determined by the uncertainties of the measurements of temperature and mass and the value for specific heat capacity. The estimation of an overall uncertainty from its component parts is called “**combination of uncertainties**, or “**error analysis**”.

2. Basic rules for propagation of uncertainties

These are simplifications that lead to a close approximation of the uncertainty

1) addition and subtraction: Rule = add uncertainty

Example : Initial temp = 34.5 °C (± 0.05) Final temp = 45.2 °C (± 0.05)
So temperature change = 45.2 – 34.5 = 10.7 °C (± 0.05 + 0.05 = ± 0.10 °C)

2) Multiplication and division : Rule = calculate relative uncertainties, add them and then convert back to absolute uncertainty

Example : Mass = 9.24g (± 0.005g) Volume = 14.1 cm³ (± 0.05cm³)

Density = 9.24 / 14.1 = 0.655gcm⁻³

Uncertainties are Mass .005/9.24 x 100 = 0.054% and Volume = 0.05/14.1 x 100 = .35% So adding uncertainties gives us 0.40%

Hence we have density = 0.655gcm⁻³ ± 0.40%

It would be more correct to calculate the absolute uncertainty from this relative uncertainty as follows:

0.655 x 0.40/100 = 2.62 x 10⁻³ ... So we have 0.655gcm⁻³ ± 0.003

3) Multiplying or dividing by a pure (whole) number; Rule : multiply or divide the uncertainty by that number

Example: 4.95 ± 0.05 x 10 = 49.5 ± 0.5

It does not take long to realize that the calculation of uncertainty can make a simple problem far more complex! I for one do not expect students to do an uncertainty calculation at every opportunity, BUT I do

tell them when we do a lab where these calculations can be performed easily and where they are most relevant...ie where there is a known answer and one wants to do a good evaluation.

C. Examples of uncertainties and errors in Conclusion and Evaluation

Example 3: Calorimetry investigation:

$$T_f = 24.2 + 0.2 \text{ C}$$

$$T_i = 21.5 + 0.2 \text{ C}$$

$T = 2.7 + 0.4 \text{ C}$; **note:** in addition and subtraction, the uncertainties are added together.

$$Q = mc \Delta T = 200\text{g} \times 4.18 \text{ J g}^{-1} \text{ C}^{-1} \times 2.7 \text{ C}$$

= 2257 J (more than the minimum number of significant figures are carried here as this is an intermediate calculation)

If this temperature rise is due to the reaction of 0.0500 mol acid that is added to 0.0500 mol base, then enthalpy of neutralization, H is:

$$H = - \frac{2257}{0.0500} = -45.1 \text{ kJ mol}^{-1}$$

(Note the correct use of significant figures)

If the accepted value for this reaction is $-56.2 \text{ kJ mol}^{-1}$, the percentage difference, or percent error, is:

$$\frac{56.2 - 45.2}{56.2} \times 100 = 19.6\%$$

The percentage estimated uncertainty in the temperature reading ($T = 2.7 + 0.4 \text{ C}$), on the other hand is:

$$\frac{0.4}{2.7} \times 100 = 15\%$$

Assuming that the uncertainties in m , c , and n (the amount of acid or base) are negligible, then: The % error (19.6%) is **greater** than the % uncertainty in the reading due to random errors. (if percent uncertainties were available in m , c , and n , then in operations of multiplication and division, % uncertainties are added to give overall % uncertainty – see example 2 below for the Determination of F , the Ideal Gas Constant). Since the % uncertainty of 15% is **less** than the % difference of 19.6%, then random errors alone cannot account for the difference between the experimentally determined value and the literature value. Systematic errors **must** have contributed to the difference. The student would then try and identify systematic errors that make suggestions to improve the investigation in Conclusion and Evaluation. The same sort of analysis can be undertaken if the experiment is repeated and an experimental uncertainty is obtained. Let us suppose that the same experiment was done three times, and that the values for

the three trials were 45.1, 43.7, and 46.5 kJ mol⁻¹. This gives an average value of 45.1 kJ mol⁻¹ and an average deviation of 0.9 kJ mol⁻¹. The percent average deviation is 2%. This is much smaller than the estimated uncertainty and percent error, indicating that the experiment was carried out with good precision, but a substantial systematic error. Further discussion should explore possible sources of error, especially those which could give a low value.

Example 4: Determination of R, the Ideal Gas Constant, using the equation $R = \frac{pv}{nT}$

The data below include the percentage uncertainties in each of p, v, n, and T determined in a particular investigation where nitrogen gas is collected by displacement of water:

$$P_{N_2} = 98.1 + 0.23\% \text{ kPa}$$

$$V_{v1} = 0.363 + 0.55\% \text{ dm}^3$$

$$n_{N_2} = 0.0147 + 1.05\% \text{ mol}$$

$$T_{N_2} = 298.8 + 0.07\% \text{ K}$$

The total estimated uncertainty = 0.23 + 0.55 + 1.05 + 0.07 = 1.90% = 2%

(Uncertainties are meaningful only to one significant figure.)

$$R = \frac{pv}{nT} = \frac{98.1 \text{ kPa} \times 0.363 \text{ dm}^3}{0.0147 \text{ mol} \times 298.8 \text{ K}} = 8.11 \text{ kPa dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

The percentage difference between the literature and experimentally determined value is:

$$\frac{8.314 - 8.11}{8.314} \times 100\% = 2.45\%$$

Since the % difference is **greater** than the % uncertainty, then random errors alone cannot account for the % difference, and there **must** have been systematic errors in the investigation. The student would then identify and systematic errors that could be responsible for the value of R being lower than expected and make suggestions to improve investigation under the Conclusion and Evaluation criterion.

On the other hand, if the value of R were within 2 % of the literature value, i.e., between 8.15 and 8.48, then the % difference would be less than the 2 % uncertainty. In such cases the % difference is not significant and can be explained by random errors alone in reading the scales of the instruments, and there is no reason to doubt that the value of R is 8.314 dm³ kPa K⁻¹ mol⁻¹.