

## Oxford University Chemistry Practical Course

### 1<sup>st</sup> year physical chemistry

#### X.2 An Introduction to Experiment design and Experimental Error

##### Introduction

This experiment is one of several that lay the foundation for the more advanced experiments to come in the second and third year of the practical course. These 1st year experiments introduce you to, or remind you of, some fundamental ideas – experimental or theoretical – that are of widespread value in chemistry.

During this experiment on data analysis, you will carry out several mini-experiments that will yield different types of data for you to analyse; you will then use the data to investigate how reliable your results are. You will also get some practice in simple experiment design, when you have an experimental goal but are not given detailed instructions on how to achieve that goal.

##### Before starting work

Read through all of the first part of these instructions, which provides background information. Also read the background material on errors contained elsewhere in this manual. There will probably be several groups of students tackling this experiment at the same time as you and there is only one set of equipment for some parts of it. Therefore, although you must complete all parts of the experiment, you may not be starting with experiment A. If you are using:

set 1 start at exercise A,  
set 2 start at exercise C,  
set 3 start at exercise E,  
set 4 start at exercise G,  
set 5 start at exercise I.

##### Why do you need to know about errors?

Suppose that during an experiment you have taken several measurements. If you have taken many readings, it might be easy to tell whether your data are precise or not, but how can you tell how reliable those readings are? What if you were able to take only one reading, a melting point perhaps; is it possible to know how reliable it is? And if you have made several repeat measurements of the same property, how should you analyse them in a mathematically sound way? Answering such questions takes us into the field of error analysis which is at the core of this experiment. It is essential to make a sound analysis of your data, but in general this is not complicated. You will need just to apply a few rules (and think a bit!).

Let's look at an example where knowing how good your results are allows you to determine whether the experiment has been a success or not.

You perform an organic synthesis, nitrating toluene in a mixture of concentrated nitric and sulphuric acids. The product might be o-nitrotoluene, m-nitrotoluene or p-nitrotoluene, so to identify it you measure the boiling point; it is 228.5 °C.

You check the boiling points of the three isomers and discover they are o: 225°C, m: 230-231°C and p: 238°C. Which isomer have you made? It all depends upon the error in your measurement. If the error<sup>1</sup> were  $\pm 2$  C your result would be consistent only with the m-isomer. However, if you estimated that the error might be  $\pm 4$  C, your measurement does not allow you to distinguish between the o- and the p-isomers. (If the error were just 1C, your reading would not be consistent with the boiling point of any of the three isomers; you might conclude that the synthesis had failed, the sample was contaminated, that you had obtained a mixture of isomers or that the measurement itself was perhaps not as reliable as you had thought.)

This example shows that merely taking a measurement without assessing the error that it may contain is possibly misleading, and is certainly poor science.

In any experiment you can anticipate there may be both *random errors* and *systematic errors*. Random errors are unpredictable and unavoidable; for example:

1) After carrying out a synthesis, you divide your product into three portions and measure the melting point of each one. Although all samples are from the same batch, you will probably find that the melting points differ slightly, because you have not read the apparatus in exactly the same way each time, or your judgement of when the sample melts varies.

2) You weigh several identical standard 10g weights on a sensitive balance. As a result of fluctuations in temperature, air currents across the top of the balance, or moisture from your fingers on the weights the reading changes slightly from one weight to the next.

3) You use a Geiger counter to count the number of radioactive particles emitted per minute from a sample of carbon-13. Radioactive decay is inherently unpredictable, so, although the average count rate is approximately constant, the number of counts that you record in successive short periods of time is not.

By contrast, *systematic errors* produce a constant error which has the same effect<sup>2</sup> on every reading; examples include:

1) You use a pipette to measure out 10 ml liquid. Unknown to you, the calibration of the pipette has been printed in the wrong place on the pipette, so the volume of liquid dispensed is too low by 0.1 ml each time you use it.

2) You measure the pressure, volume and temperature of several samples of carbon dioxide and use the ideal gas law to determine the number of moles of gas in each sample. You were not aware that carbon dioxide does not follow the ideal gas law very well at room temperature, so your results contain an error because you were using an approximate equation for your calculations, but thought that it was exact.

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<sup>1</sup> In other words, the minimum and maximum values consistent with your measurement are 226.5 C and 230.5 C.

<sup>2</sup> The error need not be the same size every time though. For example, a graduated pipette might be miscalibrated because the calibration marks have been printed incorrectly; every reading might be wrong by a constant volume of, say, 0.5 ml. On the other hand, the internal bore of the pipette might be of the wrong diameter. In this case, all volumes delivered by it are likely to be out by roughly the same fraction, so the volume error will grow as the volume delivered is increased.

There is a third type of error, the blunder, which nearly all of us come across at some stage (some more frequently than others).

The balance you were using reads 27.216g and you record this as 27.612g, or the instructions for an experiment call for ferrous sulfate and you use iron (III) sulfate.

Beyond trying to work carefully, there is little you can do to avoid blunders (apart from, perhaps, choosing a good lab partner ...) and we shall not consider them further in this experiment.

## How to complete the experiment

The instructions to the experiment are not as explicit as you may have been used to at school. This is because we would like you to think about how to work, not just follow some pre-set plan. Therefore, for most of the exercises, you will be told what needs to be accomplished, but not how to accomplish it. Before starting each exercise discuss with your partner how you might achieve the goal; if you have no good ideas you may consult the demonstrator, but try to come up with your own ideas whenever possible.

### Experiment A: Error in the use of burettes (Upper lab)

#### The experiment...

When you use a burette to measure the volume of liquid during a titration you cannot, of course, be sure that you can add exactly 1.0000 ml or some other precisely-defined amount. Devise an experiment to determine how accurately you can measure a volume of liquid using a burette. Before you start, estimate what you think the error in your measurements might be.

Discuss with your lab partner how you will do this and how to analyze the data you obtain. If you are unsure how to proceed, talk with others who are doing the experiment or a demonstrator.

#### The write-up...

When finished, describe your experiment in your data book *in a couple of sentences*. Also comment on the following points (only a line or two should be needed – do not write an essay):

- (i) the presence and size of any random error;
- (ii) is there any evidence of systematic error? If so, what is that evidence? (remember, the burettes might have been damaged by other students, or even deliberately altered by those running the practical course).
- (iii) the origin of any random error;
- (iv) the origin of any systematic error you have identified;
- (v) would your deduction be different if you had done the experiment a large number of times?

### **Experiment B: Error in the use of pipettes (Upper lab)**

#### **The experiment...**

Repeat Experiment A using a pipette. Once again, estimate in advance how good you think that your measurements will be.

#### **The write-up...**

Very briefly comment on the same factors as in Experiment A.

### **Experiment C: Wooden balls (Upper lab)**

#### **The experiment...**

You are provided with a large number of small wooden balls. The balls are made from two different woods, so on average have different densities. Devise an experiment that would allow you to determine the weight of each type of ball, bearing in mind that the densities of the two woods may not be very different and that not every ball, even made from the same wood, will be identical.

#### **The write-up...**

Describe briefly what you have done and quote results and conclusions. If you have weighed balls individually, describe what would be the outcome if instead you were forced to weight balls in groups of, say, eight. Could you still determine an average weight for each type of ball? Are there any experiments that you can recall that rely upon a similar principle?

### **Experiment D: The half-life of a Light stick (Upper lab)**

#### **The experiment...**

You have one light stick. Suppose that you wanted to measure the half-life of the light output from this light stick (the time required for the light output to fall by one half), but had no dark room in which to do so, so had to measure the amount of light out in the open laboratory.

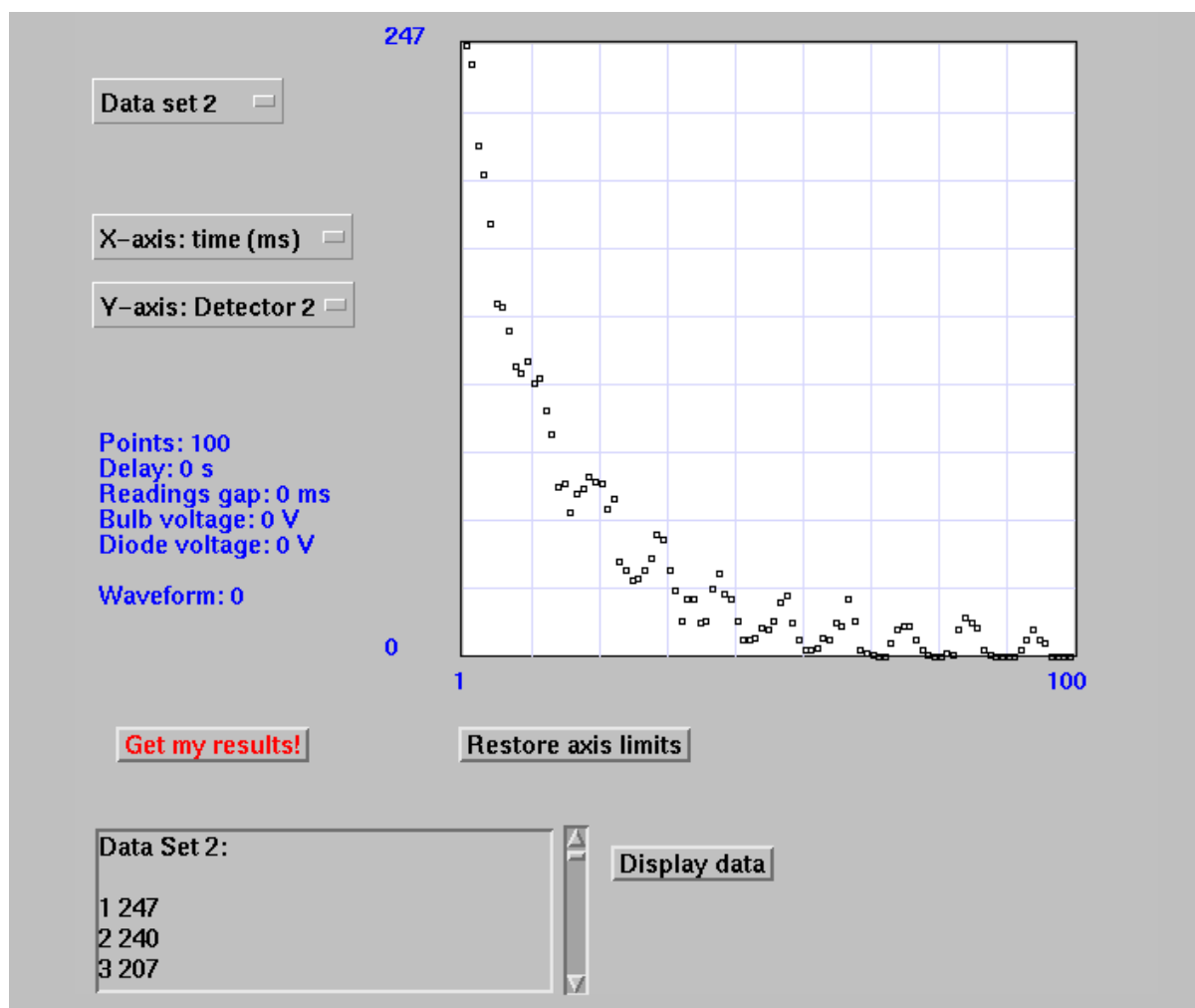
What factors would make this difficult? Would you expect that any measurement of the half life of the light stick (the time required for the light output to fall by a factor of two) would be less accurate in the open laboratory than in a dark room? With your single light stick determine the light output both when the stick is protected from the light and when it is in the open laboratory.

#### **The write-up...**

Explain *briefly* how you found the half-life for the light stick both in the dark and in the open laboratory. Comment on how reliable you think your results are.

## Experiment E: Calculating errors (Either lab)

The experiment...



The figure shows the decay of a small phosphorescent (light-emitting) sample over a period of one hundred milliseconds.

The write-up...

Calculate the rate constant for the decay, which is 1<sup>st</sup>-order<sup>3</sup>. Estimate the uncertainty in the rate constant, then calculate the half-life for the decay and calculate also the error in the half life. Comment on the fluctuations in the light output that are evident in the figure.

<sup>3</sup> In a first order reaction the light output decays exponentially with time, and the constant in the exponential is the rate constant. Devise a suitable plot to allow you to determine this constant. If in doubt, consult a demonstrator.

### **Exercise F: Beer's law (Upper lab)**

#### **The experiment...**

As white light passes through a coloured solution, light of particular wavelengths is absorbed; quite reasonably, the more solution there is, the more the light is absorbed.

Devise an experiment to determine how much light is absorbed by solutions of different concentration. You have available stock solutions of several different colours; use only one colour of solution.

#### **The write-up...**

What assumptions have you made during the experiment? Can you determine what the relationship is between the amount of light passing through the solution and the concentration?

Make a sketch that shows how the number of photons changes as white light passes through a coloured solution. Can you use this to devise a law that links absorption to concentration?

### **Exercise G: Finding pi (Lower lab)**

#### **The experiment...**

It is possible to determine the value of pi experimentally in a simple way, using small pieces of paper and a diagram on which both a circle and a square appear. Devise and perform an experiment to do this, using, if you wish, Appendix 1.

#### **The write-up...**

Report the results of your experiment. Comment on how the experiment would have to be performed in order to get a value for pi that is likely to be within 1% of the correct value.

### **Exercise H: Fluorescent tubes (Upper lab)**

#### **The experiment...**

How much light is given out by one fluorescent tube in the laboratory compared to the total light output of the sun? Devise and perform an experiment to calculate this.

#### **The write-up...**

Comment on the sources of error in the experiment. Given that the fluorescent tubes have a rating of 20W, what assumptions would you need to make in order to determine how many photons per second are emitted by the sun, assuming that the spectrum of the sun is the same as that of a fluorescent tube?

### **Exercise I: Uncertainty in repeated experiments (Upper lab)**

#### **The experiment...**

Dissolve 1.5g sodium hydroxide in 50 ml water (wear safety glasses). Dissolve 4g glucose in 150 ml water and add to it a little indigo carmine. Mix the two solutions by tipping from one beaker to the other several times and note the resulting colour.

Leave the beaker containing the solution on the bench and determine how long it takes for the colour to change to gold (this will be between five and ten minutes). Once the colour has changed to gold, pour the liquid repeatedly from one beaker to the other and determine how many transfers from one to the other are required to regenerate the colour that was formed when the liquids were first mixed.

(Note that the solution is both caustic and slippery, so hold the beakers carefully. Be careful not to get the liquid on your skin or in your eyes. If you do come into contact with the solution, wash it off with water immediately. Report any eye contact to a demonstrator immediately.)

#### **The write-up...**

- (i) Explain why you think the colour changes occurred.
- (ii) Record the time and number of transfers required for the colour changes.
- (iii) Compare your results with other groups who have done the experiment on the same day. The results could in theory be used to determine a reaction rate. What sorts of measures would you take to get a rate in which you could have a reasonable level of confidence?

### **Exercise J: Combining errors (Upper lab)**

#### **The experiment...**

Determine the density of the metal plate provided.

#### **In your databook...**

Use the information supplied in the background material to determine a reasonable estimate for the error in your result. What factors contribute to the error?

### **Exercise K: Radioactive decay (Upper lab)**

#### **The experiment...**

Use the equipment supplied to determine the rate of radioactive emission from the sample supplied.

#### **In your data book...**

Determine the mean count rate. Estimate the total number of disintegrations per second. Compare your experimental estimate of the activity of the sample with its original activity (this is noted in the box that holds the samples). Calculate how much the activity has fallen since purchase and hence how long ago the sample was bought.

**Appendix 1**

