

Experimental Physical Chemistry

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Preface

There is a danger that the experimental course of any chemistry department becomes its Cinderella—outdated, unloved, and clothed in drab apparel. Any author who has the temerity to produce a book for the prevention of such calamity must explain his philosophy, and how it is translated into print.

Most of my comments will be directed towards staff and students in colleges, polytechnics, and universities. First, however, a word to school-teachers. One or two of the experiments in this book have been published already, and the response from schools has been enthusiastic. Particular interest has been shown in the computer titration experiment (4.6) and the Brownian motion experiment (7.1). A number of other experiments should be of interest to schools, and are labelled with a letter A in the contents list. They may require obvious simplification of their theory.

What, then, of philosophy? Essentially, a laboratory course in physical chemistry should teach a range of practical skills which are generally considered relevant to a modern approach to the subject, and which will be of use to a student who wishes to apply his learning to his career. I have scrapped or ignored many experiments which I feel do not meet this requirement, and have included studies which give practice in the simple preparation and observation of solutions, the use of microscopes, glass-blowing, the operation of vacuum lines, the use of spectrometers, and many other skills.

To speak of a modern approach to the subject implies that the experiments should reflect current trends in physical chemistry, and the two most evident developments are in the use of lasers and computers. Lasers present a safety problem, but, by dint of numerous safety interlocks, we have a laser Raman experiment running in the department at Oxford, which I have included (Expt 5.8). With regard to computers, perhaps the most dispiriting aspect of their use in practical courses is as inscrutable machines which magically devour imperfect results and convert them to impressive multi-coloured graphs. Clearly laboratories should have a range of package programs available, and computer programs should be used where the calculation of results by electronic calculator is virtually impossible (Expts 5.4 and 8.5) or very tedious (e.g. Expts 6.2 and 8.6). Apart from this they should be treated with suspicion unless they enhance the experiments and teach new skills. Three experiments

have been introduced with this positive aim in mind. The first, Expt 4.6, involves the programming of a microcomputer in BASIC to operate a simple auto-titrator. As the students themselves have pointed out, once the programming has been done, the automation allows them some time to sit back and think about the chemistry involved. In addition there are two experiments which involve computing alone. One is the calculation of conformational energies by extended Hückel theory, in which students have to format the input data, and process the output data to answer several questions about the structure of simple molecules (Expt 5.13). The other (Expt 7.2) is the simulation of phases by molecular dynamics, in which students have to write a simple routine to describe the interactions between molecules. Computer programs for all seven of the experiments mentioned are available from the author.

The idea of modernity leads to my next point, which is that a practical course should relate to the courses which are currently taught as physical chemistry. There would be little point, however, in my repeating experiments from other textbooks on the subject, although the reader will notice that I have not avoided such overlap entirely. To satisfy both these conditions and the criteria mentioned earlier, I have scoured many departments, and here present my own selection of 51 experiments gleaned from polytechnic and university departments of physics, chemistry, and chemical engineering, at thirteen different centres in this country, the United States, and Australia. A further eight experiments have been specially developed with this book in mind.

Nevertheless the selection of experiments presented in this book is open to further improvement. I do not believe that surface chemistry, for example, is well served solely by Expts 2.9 and 2.10. Advanced experiments using specialist, expensive items of apparatus also present a problem. Such experiments tend to be specific to the apparatus in use. Furthermore the existence of the apparatus in the department implies that there is a member of staff with the expertise to use it, who may not be greatly assisted by a text such as this. To ignore advanced experiments entirely, however, would be to betray their importance. Thus I have chosen to include nuclear magnetic resonance, light scattering, laser Raman and mass spectrometry, but have excluded interesting experiments involving rotating disc electrodes, X-ray scattering, neutron activation analysis, electron-spin resonance spectroscopy, and photo-electron spectroscopy.

Finally, much thought has been put into the ordering and structure of the experiment scripts themselves. Students walking with trepidation into a strange laboratory are often discouraged when they pick up instructions which plunge them into unknown areas of their curriculum. A number of measures have been taken to introduce the subject in an interesting way. The most visible is the use of marginal notes, which I hope will enliven the text without detracting from it. Secondly, I have attempted to group

the experiments imaginatively. Each of the sections has an introduction to put the experiments into context, and to give a brief idea of the experimental skills taught or required, and the type and level of the theory involved. Each experiment script has an introductory section of its own, shedding further light on these matters, and explicitly stating the purpose of the experiment. The *Theory* section which follows is intended to enable the student to understand the derivation of the working equations, and to relate the experiment to accounts from textbooks, lectures, or classes. It is designed to be read on the laboratory bench, and the approach and notation has therefore been simplified as much as possible. Only when the experimental results demand it do the discussions and equations verge on rigour. The use of Appendices is minimal, since in the laboratory environment they are often ignored. The *Apparatus* section details the instruments and devices that are used to investigate the phenomenon which has been discussed. The *Procedures* are intended to be reasonably general, but asterisks (*) are used to indicate where further information must be sought or supplied. After the *Calculation* is a *Results* section which is intended to give guidance to students, who may then feel less bound to consult a previous 'correct' account, and which is also intended to help instructors when they are setting up and testing the apparatus. The *Technical notes* are also designed to assist instructors and technicians. The apparatus lists which they contain include \$ signs to indicate expense, or in the case of \$\$, considerable expense, and also † signs which indicate that the apparatus can be set up by an enthusiastic amateur, or, in the case of ††, by a skilled technician. The items in square brackets may not be required. Finally there are references which do not for the most part refer to general texts, except where they are particularly apposite, but do indicate the source of the experiment, further and more rigorous theory, and the source of any data.

The reader will notice the absence of techniques experiments and projects. Active consideration has been given to experiments which are purely designed to teach practical techniques, but there are difficulties, as has been found both at Oxford and in other departments. The problems are enshrined in requests of the type: 'Go and play on that obsolete vacuum line until you're confident you won't wreck this one'. Projects are also difficult to encompass in a book of this nature, because they are so often the province of specialist interest.

In the production of this book each experiment has been sought out or developed from scratch, redrafted or rewritten entirely, tried on students, and circulated to experts in the field. Such a task, which at times seemed of a magnitude which threatened to engulf me, would not have been remotely possible but for the able and willing assistance of a great many people. First I must thank Dr W. G. Richards, who proposed the idea of this book, and who has been a source of encouragement throughout its development. I am indebted to Professor J. S. Rowlinson for his permis-

sion for me to use my departmental position and the resources of the department as the corner-stone of the book, and I am grateful to both Professor Rowlinson and Professor I. M. Mills for their advice on the book in its entirety. I also thank Dr P. W. Atkins and Dr E. B. Smith for their views on format and the approach to the subject of experimental physical chemistry.

I am grateful to Dr R. Compton, Dr E. B. Smith, and Dr M. J. Pilling for reading entire sections. I also thank the following, whose assistance has ranged from single items of advice to the development of entire sets of experiments: W. J. Albery (Imperial College, London), M. P. Allen (Oxford), R. R. Baldwin (Hull), R. F. Barrow (Oxford), R. J. Bishop (Kingston Polytechnic, London), A. Callear (Cambridge), M. S. Banna (British Columbia, Canada), C. J. Danby (Oxford), J. Eland (Oxford), D. H. Everett (Bristol), R. Freeman (Oxford), R. P. H. Gasser (Oxford), R. Greet (Southampton), G. Hancock (Oxford), A. Hamnett (Inorganic Chemistry, Oxford), T. Hardman (Reading), J. Hatton (Physics, Oxford), D. F. Klemperer (Bristol), J. D. Lambert (Oxford), K. A. McLauchlan (Oxford), G. C. Maitland (Chemical Engineering, Imperial College, London), R. B. Moodie (Exeter), D. H. Napper (Sydney, Australia), A. D. Pethybridge (Reading), R. Popplewell (Oxford), I. Powis (Oxford), W. G. Richards (Oxford), G. Saville (Chemical Engineering, Imperial College, London), D. P. Shoemaker (Oregon, U.S.A.), J. Shorter (Hull), C. J. S. M. Simpson (Oxford), L. E. Sutton (Oxford), F. L. Swinton (Coleraine, N. Ireland), R. K. Thomas (Oxford), D. J. Tildesley (Southampton), C. F. H. Tipper (Liverpool), D. W. Turner (Oxford), B. Vincent (Bristol), R. W. Walker (Hull), R. P. Wayne (Oxford), J. le P. Webb (Sussex), J. W. White (Oxford), and D. A. Young (Chemical Engineering, Imperial College, London). I must also thank the following research students for their very considerable contributions: W. P. Baskett, D. J. F. Chaundy, M. A. Cordiero, A. R. Tindell, and J. R. P. B. Walton.

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My final thanks must go to the scores of undergraduates who have been so keen to test the new experiments, and whose enthusiasm for the project has been my ultimate reward.

Plymouth Polytechnic
September 1984

G. P. M.

List of symbols

Listed below are the most common meanings of the symbols used in this book, which are not necessarily given in the text when the usage is unambiguous. Further specific meanings, limited to single experiments, are defined at their first occurrence.

Symbol Meaning

a	activity, absorptivity
aq	aqueous solution
A	area, Debye-Hückel constant
b	Langmuir constant
B	second virial coefficient, magnetic field strength, brightness, rotational constant
B'	second virial coefficient of pressure series virial equation
c	concentration, speed of light in vacuum, intercept of a straight line
C	third virial coefficient, number of components, capacitance, count rate
C'	third virial coefficient of pressure series virial equation
C_p	heat capacity at constant pressure
C_v	heat capacity at constant volume
d	diameter
d	<i>in calculus</i> a limitingly small change
D	diffusion coefficient, centrifugal distortion constant
e	electronic charge, emissivity
e	base of natural logarithms (≈ 2.7183)
E	potential difference (e.m.f.), electric field intensity, energy, probable error
E_a	activation energy
E^\ominus	standard electrode potential
E^\ominus'	formal redox potential
f	force, function
F	number of degrees of freedom, viscous force
g	gas
g	acceleration due to gravity, gyromagnetic ratio, degeneracy
G	Gibb's free energy, vibrational term value, conductance
h	Planck's constant, height
\hbar	$h/2\pi$
H	enthalpy, Hamiltonian operator

i	$\sqrt{-1}$
i	current
I	moment of inertia, intensity of radiation, ionic strength
j	total angular momentum quantum number
J	rotational quantum number, coupling constant, flux
k	rate coefficient
k_B	Boltzmann constant
K	equilibrium constant, rotational quantum number
K^\ominus	standard equilibrium constant
K_f	cryoscopic constant
K_p	equilibrium constant in terms of partial pressures
K_{sp}	solubility product
l	liquid
l	length, orbital angular momentum quantum number
ln	natural logarithm
\log_{10}	logarithm to base 10
L	Avogadro's constant
m	mass, molality, mean, gradient of a straight line
M	molar mass (molecular weight), molarity
M	mol dm^{-3}
n	number of moles, refractive index, <i>in spectroscopy</i> number of molecules
p	pressure, permanent electric dipole moment
pH	$-\log_{10}(a_{H^+})$
P	probability, number of phases, polarization
q	heat absorbed by system, partition function for an isolated molecule, charge
Q	vibrational co-ordinate
r	radius, relative density
R	gas constant, resistance
\mathcal{R}	Rydberg constant
s	solid
s	solubility, spin quantum number
S	entropy
t	time, transport number
T	thermodynamic temperature
U	internal energy, potential energy
v	velocity, vibrational quantum number
V	volume, voltage
w	work done on system
W	mass
x	mole fraction
z	number of charges
Z	collision frequency factor
α	degree of dissociation, optical rotation, polarizability, transfer coefficient

γ	activity coefficient, surface tension, C_p/C_v , magnetogyric ratio
γ^*	mean ionic activity coefficient
δ	<i>in calculus</i> a very small change, chemical shift, film thickness
∂	<i>in calculus</i> a partial differential (i.e. a differential with one or more other parameters held constant)
Δ	<i>in calculus</i> a finite change, <i>in thermodynamics</i> the change in a thermodynamic function from one state to another
ϵ	molecular energy, dielectric constant, permittivity (Expt 5.2) or relative permittivity (Expt. 6.3), decadic extinction coefficient, well depth
ϵ_0	permittivity of a vacuum
ϵ_r	relative permittivity
η	viscosity coefficient, overpotential
θ	surface coverage, angle
κ	electric conductivity, Napierian extinction coefficient
λ	wavelength, ionic conductivity, mean free path
Λ	molar conductivity
Λ_0	molar conductivity at infinite dilution
μ	chemical potential, reduced mass, magnetic moment
μ_{JT}	Joule-Thomson coefficient
ν	frequency, <i>in statistics</i> degrees of freedom
$\bar{\nu}$	wavenumber
$\bar{\xi}$	average deviation
π	osmotic pressure
\prod	product
ρ	density, radius of gyration
σ	standard deviation, charge per unit area, shielding constant, collision diameter
Σ	sum
τ	relaxation time, chemical shift, transmittance
ϕ	electric potential, orbital
Φ	quantum yield
χ	atomic orbital
χ^2	distribution of goodness of fit
ψ	wave function
ω	vibrational wavenumber
Ω	omega integral
*	<i>in instructions</i> seek or supply further advice; <i>in calculations</i> a reduced (dimensionless) quantity
†	can be set up by enthusiastic amateur
††	can be constructed by skilled technician
\$	expensive
\$\$	very expensive
[]	<i>in chemical equations</i> concentration; <i>in Apparatus lists</i> optional item

Reports

Students often regard the proper writing of reports as an unnecessary chore, but entire research projects have been wasted because of poorly recorded results, and exciting new discoveries made (for example in a recent investigation into the nature of quarks) because of good documentation. There are a few cardinal rules which should be followed whichever 'house style' is adopted, and students will ignore them at their peril.

First, experiment reports should, ideally, be written directly into a robust, hard-bound book. If marking arrangements preclude this, the individual pages should at least be *securely* fastened together.

On starting an experiment, it is important that its introduction should be read first. Apart from that, the reading of the experiment script should be determined by the most efficient use of time, subject to a full ultimate understanding of the Theory and the informed completion of the investigation. It is important not to follow the Procedure blindly as one might do a recipe. A little extra effort will greatly enhance the insights gained from the experiment, will make it much more interesting, and may save a good deal of time.

The results of the experiment should be written directly into the book or page as the experiment proceeds. Consequent untidiness is much more acceptable than errors produced by copying results from tatty pieces of paper. If possible, the results should also be plotted on a rough graph during the experiment, so that there is a clear indication of the scatter of the results and whether further experiments are needed.

The calculation should be carried out as soon as the measurements are completed. The reported value of a physical quantity has little meaning unless it is accompanied by a statement of its uncertainty, and therefore at the end of the calculation there should always be an analysis of the precision, repeatability and accuracy of the results, as detailed below. A brief account of the experiment is useful, but there is clearly no point in repeating instructions in detail unless there is no copy of it to take away. The script should be checked to ensure that all questions in the text (shown in *italics*) have been answered, and that any comments in the margin have been followed up. Finally any additional comments may be added which are felt to be appropriate—what has been learned, the usefulness of the method, how it could be improved, and so on.

Errors

In this section, we discuss briefly the treatment of errors. By errors we do not mean disasters or blunders—supervisors will have their own treatment for students who perpetrate these. Instead we use the term error to describe the unfortunate tendency of any actual experimental result to be different from the true value of the parameter being measured.

Errors have three entirely different properties which should never be confused. These are their precision, repeatability (or reproducibility), and accuracy. The estimation of these properties is illustrated in the first experiment, (p. 7), and it may be helpful to refer to this example as you read the definitions which follow.

Precision is associated with the number of digits which can be meaningfully attributed to a particular measurement. Both calculators and computers have an often irritating capacity for giving out results with unrealistically high precision. A metre rule, for example, is graduated to the nearest millimetre, and even with good eyesight, which is the most direct improver of precision, it can only be read to the nearest half-millimetre. For a measured distance of the order of a metre, this corresponds to a precision of the order of $0.5/1000 = 0.05$ per cent. Suppose that we measure the diameter of a circle with our metre rule and find it to be 675 mm. We indicate the precision by writing the measurement in the form 675 ± 0.5 mm. If we multiply 675 by π to find the circumference, a calculator will give us an answer of, say, 2120.575. However, if we remember the maxim that it is impossible to extract more information from a calculation than we put into it, we realise that the precision of the circumference cannot be greater than the precision of the diameter, and that the circumference should therefore be expressed as 2120.6 ± 1.5 mm.

As computers are used more frequently, so precision is increasingly measured in bits, b . The maximum precision is $1/2^b$. In Expt 4.6, for example, we employ a convertor chip which changes analogue (continuously variable) information to digital information expressed as a positive integer. If the convertor is 8-bit, its read-out varies from 1 to $2^8 = 256$, and its maximum precision is $1/256$, or about 0.4 per cent.

The precision of a single result limits its accuracy, but with repeated measurements statistical methods may be used to gain better accuracy than precision, as described below, and electronic devices can also be employed for this purpose (p. 469).

The repeatability (or reproducibility) of a set of results is the degree to which successive readings agree with one another. The repeatability can be better than accuracy if, for example, a balance repeatedly sticks at a false balance point (p. 8).

The accuracy of a result is its degree of closeness to a true value. Provided that we have resisted the temptation of looking up the answer to

an experiment beforehand, there is no direct way in which we can find the difference between our own result and the true value. Instead we employ a well-established mixture of mathematical guidelines and informed guess-work. To be able to do this we need to understand the different types of errors and their causes.

Errors may be divided into two classes—*systematic errors* and *random errors*. Systematic errors arise from errors used in an experiment, in the method by which an experiment is carried out, or, as described below, from errors in the theory on which the experiment is based. They are often difficult to detect, but can be corrected if the source of error is known (p. xx). They may be reduced by carrying out careful experiments with good, well-calibrated apparatus, and by comparing results obtained by different methods and other workers.

Random errors can be caused by lack of precision, either in an instrument or in the way that it is read by an observer. Other causes of random errors are unpredictable fluctuations in environmental conditions, and the fundamental randomness of natural events such as radio-active disintegrations.

Each property and type of error should be dealt with separately and explicitly in the experimental report. It is also necessary to estimate how the uncertainties combine, and we shall describe these calculations after discussing the effects of inaccurate theory.

Inaccurate theory

It may not be immediately obvious why inaccurate theory can lead to errors in experimental results, and such unawareness has often led to entirely false experimental conclusions. We shall therefore discuss two examples which explain this point. The first is the measurement of standard electrode potentials, Expt 4.2. It would be very easy in this experiment to make the approximation that the activity of an ion in solution is the same as its concentration, which is equivalent to assuming that all activity coefficients are unity. Suppose that we measure the e.m.f. between a silver electrode dipping into a 1 molar solution of its ions, and a platinum electrode which has hydrogen gas bubbling around it at a pressure of one atmosphere and which dips into a 1 molar solution of acid. The approximation would lead us to believe that our measurement was the true standard electrode potential of $\text{Ag}^+|\text{Ag}$, a mistake commonly made in students' essays. However, the actual activity coefficients are considerably less than 1, as shown in Table 4.2.2 on p. 135, and to make a correct determination we must either use literature values of the coefficients, as in Expt 4.2, or find them for ourselves by making a series of determinations and extrapolating to infinite dilution, Expt 4.3.

A more subtle and therefore more pernicious danger exists in Expt 2.3, in which we measure the variation of the vapour pressure p of liquids

with absolute temperature T . The interpretation of the result is based on the Clausius-Clapeyron equation

$$\ln p = -\Delta H_{\text{vap}}/RT + \text{const.} \quad (0.1)$$

In the discussion of graphs on p. xxiv, we shall see how this equation predicts that if we plot $\ln p$ against $1/T$, we will obtain a straight line graph of slope $-\Delta H_{\text{vap}}/R$, i.e. minus the enthalpy of vaporization (evaporation) divided by the gas constant. Well performed experiments do indeed yield excellent straight line graphs, and suggest that the theory behind the equation is justified. However, if correct results do not fit a theory, the theory must be wrong, whereas if they do fit it, the theory may be correct but is not necessarily so. In this case, the good straight line graphs conceal the fact that two of the assumptions in the derivation are wrong, namely that ΔH_{vap} is constant with temperature and that the vapour behaves as a perfect gas. A straight line is produced only because these approximations cancel. But if they cancel, why worry? There are two reasons, which are quantified in the second reference quoted in Expt. 2.3 (p. 37). The first is that we do not know whether the enthalpy we are measuring is the true one or an approximation. The second is that we may be deceived into thinking that the approximations cancel under all conditions, whereas if we tried this experiment under conditions near the critical point of the liquid, the theory would break down entirely.

The two experiments we have discussed underline the fact that wherever possible, reports on experiments should include a brief, critical appraisal of the theory of the experiment.

Accumulation of errors

In a typical experiment measurements of several variables are combined to give the desired quantity. We must therefore consider how errors in the individual measurements affect the uncertainty of the final result. We first use calculus to find the expression for the general case, and then apply this to find simple expressions for the majority of the cases which we shall encounter in this book.

General case

Consider the calculations of a quantity X from experimentally observable quantities A, B, C, \dots . In mathematical terms, X is a function of A, B, C, \dots , or $X = f(A, B, C, \dots)$. The complete differential of X is

$$dX = \left(\frac{\partial X}{\partial A}\right)_{B,C,\dots} dA + \left(\frac{\partial X}{\partial B}\right)_{A,C,\dots} dB + \dots \quad (0.2)$$

$(\partial X/\partial A)_{B,C,\dots}$ represents the change in X caused by a change in A , when B, C, \dots are constant.

If the changes in A , B , etc. are finite but sufficiently small that the values of the partial derivatives are not appreciably altered, we may write

$$\delta X = \left(\frac{\partial X}{\partial A} \right)_{B,C,\dots} \delta A + \left(\frac{\partial X}{\partial B} \right)_{A,C,\dots} \delta B + \dots \quad (0.3)$$

In the case of *systematic error*, we can identify δA , δB , etc. with the absolute errors in A , B , etc. These errors can be either positive or negative. Equation (0.3) can therefore be used to estimate the total systematic error in X , which we shall call δX , from the errors δA , δB , $\delta C \dots$ associated with the observables A , B , $C \dots$.

In the case of *random errors*, on the other hand, the absolute errors in A , B , etc. can now take both positive and negative values. We can make no predictions about the sign of a random error, only about its magnitude. Consequently, any equation treating errors must be of a form which is independent of their sign. We can achieve this by squaring eqn (0.3):

$$\begin{aligned} (\delta X)^2 = & \left(\frac{\partial X}{\partial A} \right)_{B,C,\dots}^2 (\delta A)^2 + \left(\frac{\partial X}{\partial B} \right)_{A,C,\dots}^2 (\delta B)^2 \\ & + 2 \left(\frac{\partial X}{\partial A} \right)_{B,C,\dots} \left(\frac{\partial X}{\partial B} \right)_{A,C,\dots} \delta A \delta B + \dots \end{aligned} \quad (0.4)$$

Where an experiment is repeated a large number of times, it is useful to consider average errors. Equation (0.4) may be averaged, and if it is assumed that the random errors in the variables A , B , etc. are independent, the averages $\overline{\delta A \delta B} \dots$ of the cross-terms $\delta A \delta B \dots$ are zero. Our working equation therefore becomes

$$\overline{\delta X^2} = \left(\frac{\partial X}{\partial A} \right)_{B,C,\dots}^2 \overline{\delta A^2} + \left(\frac{\partial X}{\partial B} \right)_{A,C,\dots}^2 \overline{\delta B^2} + \dots \quad (0.5)$$

where now $\overline{\delta X^2}$, $\overline{\delta A^2}$, $\overline{\delta B^2} \dots$ are the mean squared errors in the variables. Because second- and higher-order terms are neglected, equation (0.5) only applies if errors are small ($\delta A/A < 0.15$).

Sums and differences

If $X = (A \pm \delta A) + (B \pm \delta B)$, or $X = (A \pm \delta A) - (B \pm \delta B)$, then

$$\left(\frac{\partial X}{\partial A} \right)_{B,C,\dots} = \left(\frac{\partial X}{\partial B} \right)_{A,C,\dots} = 1.$$

Therefore for systematic errors eqn (0.3) becomes simply

$$\delta X = \delta A + \delta B \quad \text{or} \quad \delta X = \delta A - \delta B, \quad (0.6)$$

and for random errors eqn (0.5) gives

$$\overline{\delta X^2} = \overline{\delta A^2} + \overline{\delta B^2}. \quad (0.7)$$

Products and quotients

If $X = (A \pm \delta A) \cdot (B \pm \delta B)$ or $X = (A \pm \delta A)/(B \pm \delta B)$ then for systematic errors eqn (0.3) gives

$$(\delta X/X) = (\delta A/A) + (\delta B/B), \quad (0.8)$$

and for random errors eqn (0.5) gives

$$(\delta X/X)^2 = (\delta A/A)^2 + (\delta B/B)^2. \quad (0.9)$$

Note that in this case we are dealing with combinations of *relative errors*, $(\delta X/X)$, etc.

Powers

If $X = (A \pm \delta A)^j$, then for systematic errors

$$(\delta X/X) = j \cdot (\delta A/A), \quad (0.10)$$

and for random errors

$$(\delta X/X)^2 = j \cdot (\delta B/B)^2. \quad (0.11)$$

An example of the importance of equations such as these is that the flow times of a gas through a capillary tube are proportional to the fourth power of its radius. It follows that since viscosity is directly proportional to flow time, the error in the viscosity of the gas is four times greater than the error in the measurement of the radius of the capillary tube. The radius of a capillary tube is very small and extremely difficult to measure accurately, and this relation effectively precludes the use of capillary flow viscometry for absolute measurements of gas viscosity (p. 352).

Small samples

Frequently only a small number of repetitions of each measurement are made, and in this situation we are forced to use experience and intuition to obtain reasonable estimates of their precision or uncertainty. Often this is straightforward, as in the example of the metre rule quoted earlier, while on other occasions, p. 7, it requires some knowledge of the devices in use.

Large samples

If six or more measurements of a particular quantity have been made we can, with care, interpret their values by the laws of statistics. When many more measurements have been made, it is essential to use the statistical methods which we now briefly introduce.

Statistical analysis

If the errors in a measurement are truly random, they will, in most cases, follow a *Gaussian* or *Normal distribution*. A particular case when this distribution is not followed is discussed on p. 428. The *true value* of a quantity being measured (assuming no systematic errors) is then given by the arithmetic mean of the individual measurements, provided that the number of these measurements is *very large*. The error of an individual measurement is then taken to be the difference between the measured and mean value.

The Normal distribution is a continuous distribution with probability density

$$P = \frac{\exp(-n^2/2\sigma^2)}{\sigma\sqrt{2\pi}} \quad (0.12)$$

The probability that a random error will lie between n_1 and n_2 is therefore

$$P = \int_{n_1}^{n_2} \frac{\exp(-n^2/2\sigma^2)}{\sigma\sqrt{2\pi}} dn. \quad (0.13)$$

The parameter σ is a measure of the width of the Normal error curve, and thus of the uncertainty of the measurements. It is called the *standard deviation* or the *root mean square deviation*, since it may be shown that

$$\sigma = \left(\frac{\sum n^2}{p-1} \right)^{1/2} \quad (0.14)$$

where $\sum n^2$ represents the sum of the squares of all the readings n , and p is the total number of measurements.

In an experiment where a particular measurement has been repeated many times, $p-1 \approx p$ and the standard deviation is given by

$$\sigma = \left(\frac{\sum n^2}{p} \right)^{1/2} \quad (0.15)$$

Usually, however, we only have time to make a small number of measurements, and therefore we only obtain *estimates* of the true value of the result and of the standard deviation of the measurements. When p is small, a good estimate of the standard deviation is given by

$$\sigma = \left(\frac{\sum (n-m)^2}{p-1} \right)^{1/2} \quad (0.16)$$

This expression is convenient to use, because the difference between a measurement and its mean, $(n-m)$, is smaller and easier to handle than the value of the reading itself. However, great care must be exercised in estimating σ in this way for very small values of p , since it is itself subject