The Molecular World

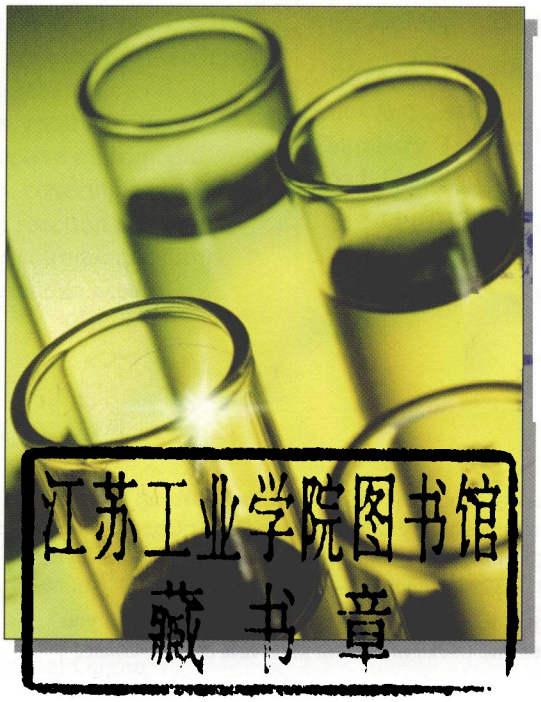
Separation, Purification and Identification

edited by Lesley Smart

The Open University

RS•C
ROYAL SOCIETY OF CHEMISTRY

Molecular World



Separation, Purification and Identification

edited by Lesley Smart

THE MOLECULAR WORLD

This book and its accompanying CD-ROMs are part of the Open University/RSC series, *The Molecular World*, which introduces Chemistry at the first/second year undergraduate level. Each book combines richly illustrated text, with questions and answers for self-assessment, and is designed for independent learning.

Part 1 *Chemistry: A Practical Subject*, deals with the common techniques used to prepare, purify and identify chemical compounds. It explains how to plan the preparation of a compound. The separation methods — distillation, recrystallization, thin-layer and column chromatography — are introduced. There is also a discussion of identification by elemental analysis, atomic absorption spectroscopy and mass spectrometry.

The practical aspects of separation and purification are presented in a series of video sequences that demonstrate the techniques and methods in use in the laboratory. In total there is over an hour of illustrative video on the CD-ROM, *Experimental Techniques*.

Part 2 *Spectroscopy*, is entirely on CD-ROM and consists of a suite of eleven programs together with self-assessment questions and summaries. The techniques of infrared, Raman, and nuclear magnetic resonance spectroscopy are taught using animations and virtual experiments to provide the underpinning for the spectroscopic theory. The reader shares in the development of the theory, and explores the interaction of radiation with molecules.

From the underlying theory the reader learns to interpret simple infrared and ^{13}C NMR spectra by constructing correlation charts. Once the correlation charts are completed, numerous spectra are provided for practice in identifying compounds.

The final program provides problems which require the interpretation of the infrared and NMR spectra for a series of unknown compounds. The solutions to these problems are entered using a molecular editor. To complete the study there is a set of interactive self-assessment questions.

The multimedia software suite comprises about twenty hours of study time in all. The multimedia programs are written in a tutorial style and provide instant feedback on correct and incorrect assignments.

The book concludes with a case study *Forensic Science*, which illustrates the use of spectroscopic techniques in providing evidence for criminal cases.

S205 Book 8

ISBN 0-85404-685-2

9 780854 046850

The Open University

RS•C ROYAL SOCIETY OF CHEMISTRY

This publication forms part of an Open University course, S205 *The Molecular World*. Most of the texts which make up this course are shown opposite. Details of this and other Open University courses can be obtained from the Call Centre, PO Box 724, The Open University, Milton Keynes MK7 6ZS, United Kingdom: tel. +44 (0)1908 653231, e-mail ces-gen@open.ac.uk

Alternatively, you may visit the Open University website at http://www.open.ac.uk where you can learn more about the wide range of courses and packs offered at all levels by The Open University.

The Open University, Walton Hall, Milton Keynes, MK7 6AA

First published 2002

Edited, designed and typeset by The Open University.

Published by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK.

Printed in the United Kingdom by Bath Press Colourbooks, Glasgow.

ISBN 0 85404 685 2

A catalogue record for this book is available from the British Library.

1.1

s205book 8 i1.1

The Molecular World

This series provides a broad foundation in chemistry, introducing its fundamental ideas, principles and techniques, and also demonstrating the central role of chemistry in science and the importance of a molecular approach in biology and the Earth sciences. Each title is attractively presented and illustrated in full colour.

The Molecular World aims to develop an integrated approach, with major themes and concepts in organic, inorganic and physical chemistry, set in the context of chemistry as a whole. The examples given illustrate both the application of chemistry in the natural world and its importance in industry. Case studies, written by acknowledged experts in the field, are used to show how chemistry impinges on topics of social and scientific interest, such as polymers, batteries, catalysis, liquid crystals and forensic science. Interactive multimedia CD-ROMs are included throughout, covering a range of topics such as molecular structures, reaction sequences, spectra and molecular modelling. Electronic questions facilitating revision/consolidation are also used.

The series has been devised as the course material for the Open University Course S205 *The Molecular World*. Details of this and other Open University courses can be obtained from the Course Information and Advice Centre, PO Box 724, The Open University, Milton Keynes MK7 6ZS, UK; Tel +44 (0)1908 653231; e-mail: ces-gen@open.ac.uk. Alternatively, the website at www.open.ac.uk gives more information about the wide range of courses and packs offered at all levels by The Open University.

Further information about this series is available at www.rsc.org/molecularworld.

Orders and enquiries should be sent to:

Sales and Customer Care Department, Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, CB4 0WF, UK

Tel: +44 (0)1223 432360; Fax: +44 (0)1223 426017; e-mail: sales@rsc.org

The titles in *The Molecular World* series are:

THE THIRD DIMENSION
edited by Lesley Smart and Michael Gagan

METALS AND CHEMICAL CHANGE
edited by David Johnson

CHEMICAL KINETICS AND MECHANISM
edited by Michael Mortimer and Peter Taylor

MOLECULAR MODELLING AND BONDING
edited by Elaine Moore

ALKENES AND AROMATICS
edited by Peter Taylor and Michael Gagan

SEPARATION, PURIFICATION AND IDENTIFICATION
edited by Lesley Smart

ELEMENTS OF THE p BLOCK
edited by Charles Harding, David Johnson and Rob Janes

MECHANISM AND SYNTHESIS
edited by Peter Taylor

The Molecular World Course Team

Course Team Chair
Lesley Smart

Open University Authors
Eleanor Crabb (Book 8)
Michael Gagan (Book 3 and Book 7)
Charles Harding (Book 9)
Rob Janes (Book 9)
David Johnson (Book 2, Book 4 and Book 9)
Elaine Moore (Book 6)
Michael Mortimer (Book 5)
Lesley Smart (Book 1, Book 3 and Book 8)
Peter Taylor (Book 5, Book 7 and Book 10)
Judy Thomas (*Study File*)
Ruth Williams (skills, assessment questions)
Other authors whose previous contributions to the earlier courses S246 and S247 have been invaluable in the preparation of this course: Tim Allott, Alan Bassindale, Stuart Bennett, Keith Bolton, John Coyle, John Emsley, Jim Iley, Ray Jones, Joan Mason, Peter Morrod, Jane Nelson, Malcolm Rose, Richard Taylor, Kiki Warr.

Course Manager
Mike Bullivant

Course Team Assistant
Debbie Gingell

Course Editors
Ian Nuttall
Bina Sharma
Dick Sharp
Peter Twomey

CD-ROM Production
Andrew Bertie
Greg Black
Matthew Brown
Philip Butcher
Chris Denham
Spencer Harben
Peter Mitton
David Palmer

BBC
Rosalind Bain
Stephen Haggard
Melanie Heath
Darren Wycherley
Tim Martin
Jessica Barrington

Course Reader
Cliff Ludman

Course Assessor
Professor Eddie Abel, University of Exeter

Audio and Audiovisual recording
Kirsten Hintner
Andrew Rix

Design
Steve Best
Carl Gibbard
Sarah Hack
Mike Levers
Sian Lewis
John Taylor
Howie Twiner

Library
Judy Thomas

Picture Researchers
Lydia Eaton
Deana Plummer

Technical Assistance
Brandon Cook
Pravin Patel

Consultant Authors
Ronald Dell (*Case Study:* Batteries and Fuel Cells)
Adrian Dobbs (Book 8 and Book 10)
Chris Falshaw (Book 10)
Andrew Galwey (*Case Study:* Acid Rain)
Guy Grant (*Case Study:* Molecular Modelling)
Alan Heaton (*Case Study:* Industrial Organic Chemistry, *Case Study:* Industrial Inorganic Chemistry)
Bob Hill (*Case Study:* Polymers and Gels)
Roger Hill (Book 10)
Anya Hunt (*Case Study:* Forensic Science)
Corrie Imrie (*Case Study:* Liquid Crystals)
Clive McKee (Book 5)
Bob Murray (*Study File*, Book 11)
Andrew Platt (*Case Study:* Forensic Science)
Ray Wallace (*Study File*, Book 11)
Craig Williams (*Case Study:* Zeolites)

CONTENTS

PART 1 CHEMISTRY: A PRACTICAL SUBJECT

Adrian Dobbs and Lesley Smart

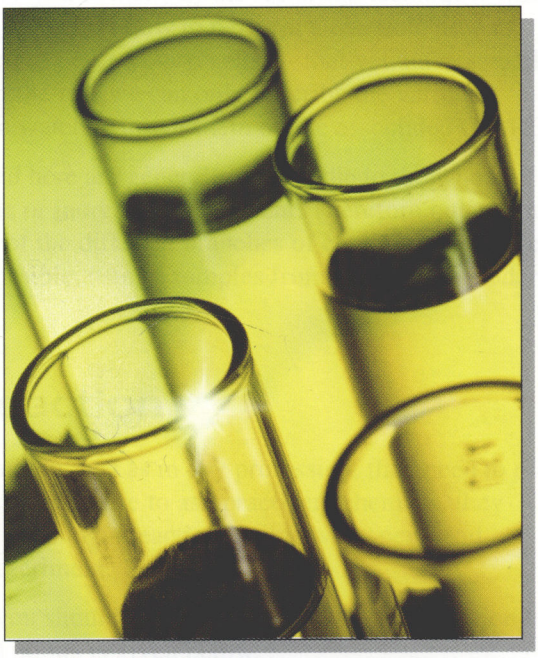
PART 2 SPECTROSCOPY

Lesley Smart and Eleanor Crabb

CASE STUDY: FORENSIC SCIENCE

Andy Platt, Anya Hunt and Lesley Smart

Part 1



Chemistry: A Practical Subject

Adrian Dobbs and Lesley Smart

based on 'The Search for Purity'
by Keith Bolton and Malcolm Rose (1991)

INTRODUCTION: PREPARATION OF A COMPOUND

1

Chemistry is a fundamental science that underpins much of the world around us. It is also a practical subject. Although much of what we have learnt so far may have seemed conceptual or theoretical in nature, the basis for it has all come about through centuries of experimental laboratory work performed originally by individuals in their own homes, but nowadays by chemists — technicians, undergraduates, postgraduates and advanced researchers. None of the chemistry that you have learnt so far would have been known without these skilled experimentalists.

The aim of this book is to introduce you to many of the skills and techniques that are required by the modern chemist, such as how to perform a reaction, how to purify the products and finally how to prove your results — that you have actually made what you set out to make. In the text we can only describe the various procedures, but you will be able to watch many of them on the associated CD-ROM.

The skills and techniques described here are generally applicable to the whole of chemistry, whether it be an organic or inorganic experiment. Therefore rather than subdividing the book on the basis of the different branches of chemistry, we have integrated the material as far as possible, using examples from all areas of modern chemistry.

1.1 Planning a reaction

Before chemists can perform a reaction, just as in any profession, they need to *plan* exactly what they are going to do. If you were to ask practising chemists, they would all agree that time spent in planning a reaction is time well spent, and invaluable to the success of the experiment.

What are the major points which you should consider when planning a reaction? A list of most of the questions and points is given below.

- The scale of the reaction — how much product do you want to make?
- The mole ratios of the reactants; how much of each reactant to use?
- How expensive are the reagents? Are there cheaper alternatives?
- What is the most suitable solvent for the reaction?
- What temperature will be required?
- How long will the reaction take?
- Will you need to work under an inert and/or dry atmosphere?
- What equipment will be needed?
- Can the reaction be performed on the benchtop, or is a fume cupboard needed?
- What safety precautions will be necessary?

You also have to consider what you are trying to achieve during the reaction. Is the reaction probing some detailed reaction mechanism or is it preparatory — in other words, part of a long synthesis directed towards a desired product. An analytical chemist investigating a mechanism will have a very different set of priorities in planning a reaction compared to a synthetic chemist.

Chemists find that the careful keeping of a laboratory notebook is essential during their work. This involves carefully noting down everything that was done during an experiment from start to finish, recording relevant masses and other data such as temperature and timings, and noting *all* observations. If this is done in an orderly fashion, then it is very easy to draw conclusions from an experiment, to draw out data for a report or publication, to repeat the reaction, or simply to plan your next reaction.

An extract from a (rather idealized!) well-kept laboratory notebook should look something like Figure 1.1.

Notice the style and the various conventions that are used. The aim of the experiment and the equation for the reaction are set out clearly at the start, followed by the method and finally the results. A note is also made of any safety precautions necessary. Note that amounts of substances are placed in brackets after the compounds they refer to and are given in grams (or mls if the compound is a liquid) and also (preferably) in numbers of moles: this is conventional for formal reports and publications, so you may as well get used to it from the start.

> Formal reports are always written in the past tense and the passive voice: '10 ml of water was added to the reaction' rather than 'I added 10 ml of water…'.

A template for how you should write-up your experiment in your laboratory notebook is given in Figure 1.2 (overleaf). You may well see variations on this style elsewhere and there is nothing wrong with most of these. However, if you follow this general format, you will not go far wrong when writing-up experiments.

1.2 Assembling the apparatus: doing the reaction

Before we can consider doing a reaction, we need to learn something about the apparatus that is available to use. You may have encountered some chemical apparatus before, for example a test tube, beaker or conical flask or even a bunsen burner. These alone however are insufficient to perform most reactions. Over the years, chemists have developed specialized apparatus for performing chemical reactions. In particular, we have glassware which is capable of withstanding extreme high and low temperatures and corrosive substances, and which can be used to keep out air and moisture. This specialized glassware consists of a series of interlocking tapered ground-glass joints (Figure 1.3 overleaf), which permit various pieces of glassware and apparatus to be connected together without the need for rubber stoppers, corks or any sort of rubber tubing connectors (the joints only need to be lightly greased). Collectively, this apparatus is known as **Quickfit® apparatus**, due to the easy and rapid way in which the apparatus may be connected and assembled.

Illustrated in Figure 1.4 (overleaf) is a typical set of glassware and Quickfit glass apparatus which you might encounter in any modern laboratory, whether it be in a university or in industry. You should try and familiarize yourself with the names and shapes of each of these pieces of apparatus, so that when you come to follow an experimental procedure, you know exactly what apparatus you need to assemble.

Title

Date

Clear diagram, showing reaction sequence being performed.
Note, also includes molecular formula and molar masses of reagents.

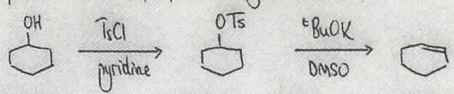
Clear calculation, laid out to show number of moles, molar equivalents and mass (or volume) for each reagent.

Some type of safety or risk assessment for the reaction, to satisfy legal requirements and show that the experimentalist has thought about the safety implications and aspects of the experiment. For particularly dangerous reactions or toxic reagents, a more detailed safety assessment may be required.

Experimental details of reaction performed, including all observable changes.

Carefully recorded mass of (each) product, together with calculated % yield(s).

Experiment to prepare Cyclohexene — 25/4/2001



$C_6H_{12}O$ (100·16) $C_{13}H_{18}SO_3$ (254·56) C_6H_{10} (82·08)

Cyclohexanol (MW: 100·16) 45·1g 0·45mol
p-Toluenesulfonyl chloride (MW: 190·65) 1·05eq. = 0·47mol = 89·8g
Pyridine 200ml
Hydrochloric acid 260ml
Diethyl ether 900ml
Cyclohexyl tosylate (MW: 254·56) 104·4g = 0·41 mol
Potassium tert-butoxide (MW 112·2) 2eq. = 0·82 mol = 92·0g
Dimethyl sulfoxide 450ml

Safety / Risk Assessment:

RISK ASSESSMENT	SUPERVISOR SIGNATURE:				
	HAZARD ASSESSMENT				
CHEMICAL	TOXIC	IRR	FLAM	CORR	OTHER
CYCLOHEXANOL	✓	✓		✓	
p-TsCl	✓	✓		✓	
tBuOK	✓	✓	✓		
Et_2O	✓		✓		
CONTAINMENT PROCEDURE: USE POWDER FIRE EXTING.					
ADDITIONAL PRECAUTIONS: KEEP UNDER INERT GAS					
OTHER NON-CHEMICAL HAZARDS: FIRE, FLOOD					
IS AN ADDITIONAL COSHH ASSESSMENT NECESSARY? YES/NO					
SIGNATURE:	DATE:				

Procedure:

Pyridine (200ml) and cyclohexanol (45·1g, 0·45mol) were placed in a clean and dry two-necked 500ml round-bottomed flask, fitted with a thermometer and under an inert nitrogen atmosphere. The flask was cooled to 0°C using an ice bath and para-toluenesulfonyl chloride (89·8g, 0·47mol) added slowly, in portions, over 20mins. The mixture was then allowed to warm to room temperature and stirred at this temperature for 16 hours. The mixture was then cooled to 0°C and added to a mixture of conc. hydrochloric acid (260ml) in ice/water (800ml) in a large flask. This was extracted with diethyl ether (3 × 300ml), the organic extracts combined, dried ($MgSO_4$) and concentrated under reduced pressure to give cyclohexyl tosylate as a pale yellow oil. Potassium tert-butoxide (92·0g, 0·82mol) was placed in a clean, dry 1L three-necked flask, fitted with a reflux condenser and dropping funnel under nitrogen, and DMSO (100ml) added. A solution of the cyclohexyl tosylate (104·4g, 0·41mol) in DMSO (350ml) was placed in the dropping funnel and added to the flask over a period of 25mins, using an ice bath to ensure the reaction temperature did not rise above 25°C. The reaction was stirred for a further 2hrs. The condenser was then rearranged for distillation under reduced pressure and the fraction boiling at ≈25°C (10-12 mm Hg) collected as the target compound - confirmed by i.r., nmr and mass spec.

Yield of Cyclohexyl tosylate:

Weight of flask + product: 371·7g
" " flask: 267·5g
" " product: 104·2g

Theoretical yield: 0·45 × 254·56
= 114·6g

% yield: (actual/theoretical) × 100/1
= 104·2/114·6 × 100/1
= 91%.

Yield of cyclohexene:

Weight of flask + product: 126·1g
" " flask: 101·4g
" " product: 24·7g

Theoretical yield: 0·41 × 82·08
= 33·6g

% yield: (actual/theoretical) × 100/1
= 24·7/33·6 × 100/1
= 74%.

Figure 1.1
An extract from a laboratory notebook.

Title	Experiment to prepare..... Date.....
Diagram of reaction including relative molecular masses/ formulae of reagents and products	
Name, relative molecular mass and amount used for each substance in reaction	
Safety/Risk Assessment	This is beyond the scope of the course, but you should be aware that any reaction requires a risk assessment to be performed prior to starting the experiment.
Method (including all masses and amounts of materials used, both in g (or ml) and mols written in past tense	
All recorded data e.g. dry TLC plate, masses and yield(s), spectroscopic data	R_f = m.t. or b.t.: IR spectra: ^{1}H NMR: ^{13}C NMR:

Figure 1.2 Template for an experimental write-up.

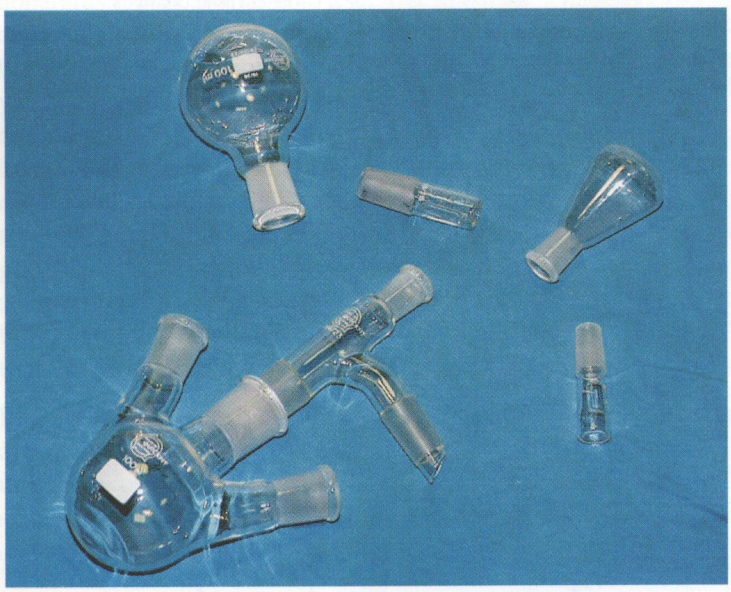


Figure 1.3
Quickfit glassware. Quickfit is a registered trademark of Bibby Sterilin Ltd.

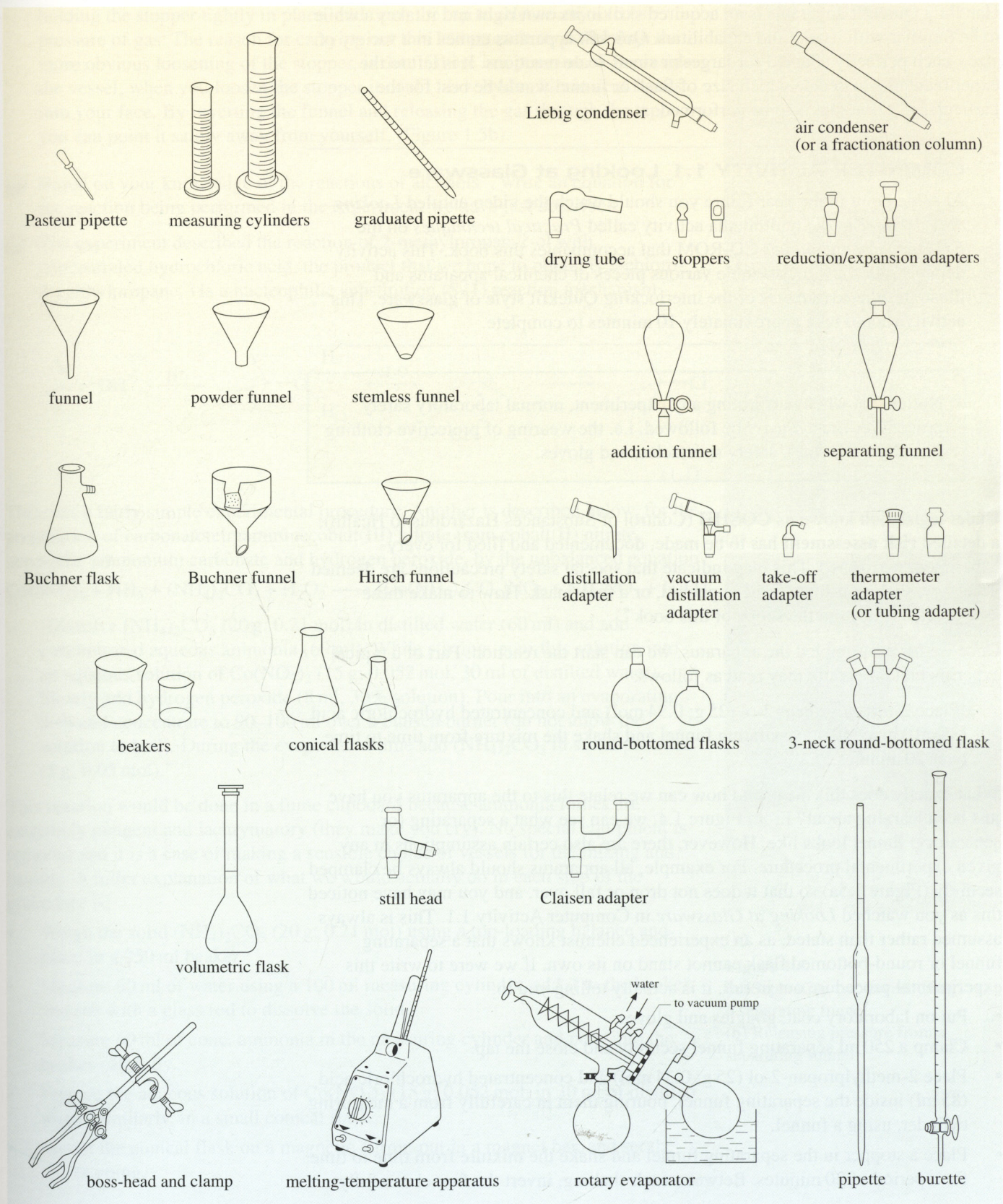


Figure 1.4 A selection of laboratory equipment.

Handling Quickfit apparatus is an acquired skill in its own right and it takes a while to be familiar with its use and capabilities. Quickfit apparatus comes in a variety of sizes, each perfectly adapted for large- or small-scale reactions. It is left to the experimentalist to decide which size of flask or funnel would be best for the particular reaction that is to be performed.

COMPUTER ACTIVITY 1.1 Looking at Glassware

At some point in the near future you should watch the video entitled *Looking at Glassware* in the multimedia activity called *Practical techniques* on the *Experimental techniques* CD-ROM that accompanies this book. This activity demonstrates how to assemble various pieces of chemical apparatus and illustrates the advantages of the interlocking Quickfit style of glassware. This activity should take approximately 10 minutes to complete.

Notice that when performing any experiment, normal laboratory safety procedures must *always* be followed, i.e. the wearing of protective clothing (usually a lab coat), safety spectacles, and gloves.

Under legislation known as **COSHH** (Control of Substances Hazardous to Health), a detailed **risk assessment** has to be made, documented and filed for every experiment performed. This may indicate that special safety precautions are deemed necessary, such as using a fume cupboard, or a face-mask. How to make these assessments is beyond the scope of this book *.

Once we have assembled the apparatus, we can start the reaction. Part of a typical experimental procedure may read as follows:

> 'Place 2-methylpropan-2-ol (25 g; 0.34 mol) and concentrated hydrochloric acid (85 ml†) in a 250 ml separating funnel and shake the mixture from time to time over 20 minutes.'

What exactly does this mean and how can we relate this to the apparatus you have just been learning about? From Figure 1.4, we can see what a separating (or separatory) funnel looks like. However, there are also certain assumptions in any given experimental procedure. For example, all apparatus should always be clamped securely (Figure 1.5a) so that it does not drop or fall over, and you may have noticed this as you watched *Looking at Glassware* in Computer Activity 1.1. This is always assumed rather than stated, as an experienced chemist knows that a separating funnel or round-bottomed flask cannot stand on its own. If we were to write this experimental procedure out in full, it is actually telling you to:

- Put on laboratory coat, goggles and gloves.
- Clamp a 250 ml separating funnel securely and close the tap.
- Place 2-methylpropan-2-ol (25 g; 0.34 mol) and concentrated hydrochloric acid (85 ml) inside the separating funnel, pouring them in carefully from a measuring cylinder, using a funnel.
- Place a stopper in the separating funnel and shake the mixture from time to time for a period of 20 minutes. Between each shaking, invert the funnel carefully,

* Risk assessments are considered further in *Exploring the Molecular World*[1].

† In practical work it is common to use 'ml' rather than the equivalent cm^{-3}.