

Introduction

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I.1. The purpose and scope of this book

The purpose of this volume is to enable a chemist to assess the possible utility of high vacuum technique for his purposes, to design and build a high vacuum system, and to do good chemistry with it. This book is not a text-book of vacuum theory, glass blowing, sophisticated analytical techniques, or anything else; it also does not deal with the techniques of gas reactions. It is not a replacement for 'Green', 'Shriver', or 'Yarwood' (see below). There is much in these, and of course in the large specialist volumes, which is not in this one.

In other words, the present book does not aim at being comprehensive in any respect, but is the best compromise the author could achieve between necessary theory and sufficient useful advice. However, here can be found numerous practical, traditional tricks and hints not found elsewhere, because the aim has been to produce a guide and companion for the worker in the laboratory.

Lest it be thought that the techniques to be described are only for the affluent institution, the author wishes to emphasise that he has only ever worked in under-funded laboratories, was brought up before, during, and after the war in a 'string-and-sealing wax' tradition, and ever heeded Lord Rutherford's exhortation to his team at the Cavendish Laboratory: 'We've got no money, boys, so we've got to think.' Very many of the author's collaborators came from or went to laboratories far better endowed than his, but were all the better for the lessons learnt in a 'do it yourself' atmosphere. That is also the reason why there are few references to sophisticated, expensive apparatus and why this book may have a slightly old-fashioned look.

I.2. Usages

I.2.1. References

The references given are simply those which are deemed most useful, and there is no pretence that they are comprehensive. The devices quoted are not the earliest nor the most famous, but generally those judged to be of the greatest use and simplicity.

Cambridge University Press

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P. H. Plesch

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I.2.2. Figures

Most of the very numerous figures are to be understood as working sketches rather than scale drawings. They should, however, be completely adequate for a glass blower to make the pieces concerned.

Invitation: If anyone is unable to make any of the pieces shown here, and cannot arrange to have it made, he should write to The Laboratory Superintendent, Chemistry Department, University of Keele, Staffordshire, ST5 5BG, England, indicating exactly what is wanted. He will then be sent a quotation for the cost of having the piece made by the Departmental glass blower.

I.2.3. Units

Throughout this work SI units have been used, with the exception of pressure, which is given in Torr. For formulae, table headings etc. the Quantity Calculus has been used, as advised by M. L. McGlashan, '*Physico-chemical Quantities and Units*', Royal Society of Chemistry Sales and Promotions Department, Burlington House, London, W1V 0BN.

I.3. Books

There are astonishingly few books which deal with the chemist's vacuum manipulations (but many for the physicist), and even those marginally connected with the subject are not numerous. Each of the books named below contains some matters of interest in the present context, but the list is certainly not comprehensive, and if a volume which is considered of value has been omitted, the author asks that it be brought to his notice.

The books which are considered useful have been listed here in alphabetical order of their authors:

- R. Barbour, *Glassblowing for Laboratory Technicians*, Pergamon Press, Oxford, 1968.
- L. Bretherick, Ed., *Hazards in the Chemical Laboratory*, 3rd Edition, Royal Society of Chemistry, Burlington House, Piccadilly, London, W1V 0BN.
- S. Dushman, *Scientific Foundations of Vacuum Technique*, 2nd Edition, Wiley, New York, 1962.
- G. W. Green, *The Design and Construction of Small Vacuum Systems*, Chapman and Hall, London, 1968.
- H. W. Melville and B. G. Gowenlock, *Experimental Methods in Gas Reactions*, MacMillan, London, 1964.
- L. M. Parr and C. A. Hendley, *Laboratory Glassblowing*, G. Newnes Ltd., London, 1956.
- A. J. B. Robertson, D. J. Fabian, A. J. Crocker and J. Dewing, *Laboratory Glassblowing for Scientists*, Butterworth Scientific Publications, London, 1957.

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D. F. Shriver and M. A. Drezdson, *The Manipulation of Air-Sensitive Compounds*, 2nd Edition, Wiley-Interscience, New York, 1986.

M. Wutz, H. Adam and W. Walcher, *Theorie und Praxis der Vakuumtechnik*, Vichweg und Sohn, Braunschweig (FRG), 1986.

J. Yarwood, *High Vacuum Technique*, Science Paperbacks and Chapman and Hall, London, 1975.

I.4. Articles

Apart from the numerous papers and articles quoted in the book itself, there are a few general ones, quoted below, which contain useful material for the purposes under consideration here. One of the earliest, and still amongst the most useful, is:

L. J. Fetters, Procedures for Homogeneous Anionic Polymerisation, *J. Res. Natl. Bureau of Standards, A. Phys and Chem*, **70A**, 421 (1966).

Some useful modern tricks can be found in:

A. L. Wayda and J. L. Dye, A Versatile System for Vacuum-line Manipulations, *J. Chem. Ed.*, **62**, 356 (1985).

Although the next item is mainly concerned with non-vacuum methods, it is worth a close look:

G. B. Gill and D. A. Whiting, Guidelines for Handling Air-Sensitive Compounds, *Aldrichimica Acta*, **19**, 31 (1986).

The following paper, which is very clear and concise, has been extensively quoted because it is not readily available in the English-speaking world:

O. Nuyken, S. Kipnich and S. D. Pask, Ueber die Manipulation empfindlicher Substanzen im Hochvakuum, *GIT Fachz. f.d. Laboratorium*, **25**, 461 (1981).

1 Fundamentals

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1.1. Reasons for using high vacuum techniques

1.1.1. Introduction

High vacuum technique (h.v.t.) is one of several types of experimental technique which can be employed to obtain a controlled experimental environment. The most usual reason for wanting this is the necessity to exclude oxygen and/or water and, less commonly, carbon dioxide from the reaction being studied. Perhaps the most primitive example of creating a controlled environment is the use of a 'soda-lime' tube to protect a store of sodium hydroxide from the ingress of carbon dioxide.

Before considering the advantages and disadvantages of h.v.t. as compared with some of the alternatives, it is important to point out that, as

with all experimental chemistry, the first questions to be answered are what information is required from the planned experiment, what level of impurities can be tolerated, and what resources are available. It is worth remembering the first two Laws of Experimentation:

- (1) What one gains in rigour one loses in flexibility.
- (2) The greater the rigour of the technique, the longer the experiment takes (the perfect experiment takes an infinite time).

Having decided that a controlled environment is needed to exclude certain normal atmospheric components, one must then decide on the levels to which concentrations of unwanted compounds must be reduced and below which they must be maintained.

There is a sequence of experimental techniques ranging from the 'open beaker on the bench' to the extremely rigorous h.v.t. used for studying the kinetics of radiation-induced cationic polymerisations. Each technique in the series has its characteristic level of extraneous materials, and as the level of 'cleanliness' is raised, there is a concurrent loss of flexibility.

If a controlled environment is necessary for the desired experiment, it is useful to examine some of the techniques alternative to h.v.t., to estimate the level of impurities involved and to assess their advantages and disadvantages as compared to h.v.t.

When contemplating the choice of technique one must keep in mind two further, highly relevant, Laws of Experimentation:

- (3) Murphy's Law: If anything can go wrong, it will go wrong. This is a very strong inducement to keep every set-up as simple as possible.
- (4) Cheops' Law: Every construction takes longer and costs more than the most pessimistic estimates.

1.1.2. The inert gas blanket

The use of a large funnel attached to a stream of inert gas situated above the bench is particularly useful when opening bottles of hygroscopic or hydrolytically unstable materials. This technique relies for its success on a fast stream of 'clean' and 'dry' inert gas. It is of course wasteful when used over long periods, but it does allow almost the same flexibility of manipulation as on the open bench.

1.1.3. Dry-bag and dry-box

The move from the open bench to a closed system involves loss of flexibility, and so a greater degree of pre-experimental planning is necessary. With careful operation, the moisture content of the atmosphere in a dry-box can be reduced to such a low level that one can do experiments in which $10^{-3} \text{ mol l}^{-1}$ of water in reagents is tolerable. To achieve this level it is important that the techniques be used intelligently, and it is worth examining

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some of the critical steps, since even when the main part of an experimental programme is to be carried out by h.v.t., it is often expedient to use a dry-box or a dry-bag for some of the preparatory stages.

Both the dry-box and the dry-bag offer a considerable degree of experimental flexibility and are very suitable for larger scale preparative work in which catalytic amounts of impurities are unimportant. However, in this context it is very important to remember that some materials, and especially natural products such as cork, wood and paper, have a high water content, however carefully they may have been dried and/or degassed, and that they should therefore never be used inside a dry-bag or dry-box.

A *dry-bag* is a bag, usually about 0.5×1 m, made of a transparent, inert and tough film or sheet which has an easily sealable entry port for inserting apparatus and several ports for admitting purging gas, electrical leads, etc., and at least two gloves so that operations can be done inside it.

The dry-bag is usually operated with a slight overpressure of the inert gas to hinder diffusion of unwanted gases into the bag. Simply running a stream of inert gas through the bag is not an efficient method of producing an inert atmosphere because the air in the lateral excrescences may take a long time to be swept out. In order to produce the inert atmosphere efficiently, the bag must be emptied and filled several times before starting the experiment. In order to find out the number of evacuation/filling cycles required to produce the desired 'controlled' environment, consider a bag having a volume of 50 l. Suppose the flattened bag has a residual volume of 1 l and the bag is then filled with 'pure' nitrogen. Since air contains some 20% of O_2 , after one evacuation/filling cycle the gas inside the bag will contain some 0.2 l of O_2 (ca. 9×10^{-3} mol at s.t.p.) and therefore the bag contains 0.4% of O_2 . A second cycle will reduce the amount of O_2 to 4×10^{-3} l (ca. 2×10^{-4} mol at s.t.p.) and the gas in the bag now contains only $8 \times 10^{-3}\%$ of O_2 . Of course, in the above calculation it has been assumed that the inert gas itself is 'pure', i.e. that its content of noxious gases is no greater than that which has been deemed tolerable for the purpose in hand, but it does indicate the level of atmospheric 'cleanliness' that can be obtained under optimum conditions. In this and in many other contexts one must remember that in relation to evacuation one is rarely, if ever, dealing with a true equilibrium, and that when the quantities of, for example, water adsorbed on glass or absorbed in organic materials (see p. 40), or volatile organic substances ad- or absorbed by rubber and plastics and greases may be of importance, only an all-glass, glass and metal, or all-metal system will be satisfactory.

The *dry-box*, also known as *glove-box*, consists essentially of a metal box with a viewing window and (at least) two rubber or plastic gloves, a port, usually with a 'lock' for the introduction of reagents or pieces of equipment, and ports for the in-flow and out-flow of inert gas, for electrical leads, etc. The atmosphere inside the box is established by a stream of well-dried and deoxygenated inert gas which is usually kept slightly above atmospheric

pressure. The dry-box, as opposed to the dry-bag, is more capacious, permanent and robust. An additional advantage is that it can be made as large as necessary. For exceptionally well-controlled experimental conditions, and additionally as a means of reducing the amount of inert gas required, the inert gas can be recirculated via an appropriate purification train. This technique has the advantage that impurities in the inert gas have less opportunity of collecting within the apparatus.

1.1.4. Vacuum lines

For smaller scale operations or when catalytic amounts of impurities are important, a vacuum line is almost always more suitable and efficient. Although it takes longer to become familiar with a vacuum apparatus, once a certain degree of competence and confidence has been achieved, there is little to choose in terms of experimental time between h.v.t. and the rigorous use of a dry-box. The choice is often made simply on the basis of laboratory tradition (i.e. inertia) and know-how.

As a reason for not using h.v.t. it is often stated that its use leads to experimental results that cannot be reproduced on an industrial scale. *This is untrue.* A closed system, such as an all-glass vacuum line, has more in common with an industrial plant than the typical apparatus used at the laboratory bench. Furthermore, because of the considerably more favourable surface to volume ratios in a large plant, the typical concentrations of those impurities which originate from surfaces are more accurately reproduced by h.v.t. experiments than by the typical bench experiment. This is often reflected in the problems encountered during development work when bench experiments are being scaled up to pilot plant and beyond.

A decision to use a vacuum line does not necessarily imply that what is here called h.v.t. must be used. The vacuum lines familiar to many inorganic chemists, and employed for many radical polymerisations differ from the all-glass high vacuum lines which are the central theme of this book, but the distinction is not rigorous. Normally, the simpler lines are used for preparative experiments in which the exclusion of oxygen and not water is the major problem. As the calculation given earlier in this section shows, if the experimental volume is evacuated between repeated fillings with an inert gas, the amount of residual gaseous impurities rapidly approaches zero.

1.1.5. Summary

The advantages of using a vacuum rather than an inert gas environment are:

- (1) Reproducibility of the experimental conditions is fairly easy to obtain. However, reproducibility of results in one set of circumstances is, by itself, no guarantee of their validity, since, especially with a vacuum line, the impurity effects can often be reproduced extremely well.

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- (2) With care, which usually means longer pumping times and greater rigour in the preparation of the experiments, the level of the impurities, such as water in liquid reagents or solvents, can be reduced to below $10^{-5} \text{ mol l}^{-1}$.
- (3) Because of the very low concentrations of water and oxygen that can be achieved, and particularly because the systems are inherently closed, it is possible to use extremely strong drying agents such as $\text{K} + \text{Na}$ or $\text{Pb} + \text{Na}$ alloys, or hot Na vapour for purifying solvents and reagents without any considerable hazards.
- (4) A particular advantage of using vacuum techniques is that liquid nitrogen can be used for the rapid freezing of materials and trapping of vapours without any danger that oxygen will be condensed out.
- (5) In contrast, the single major disadvantage of h.v.t. is that it is generally limited to work involving small volumes of material (up to 500 ml, say), although solvent reservoirs up to a few litres are often used, and the firms making near-monodisperse polymers by anionic polymerisation do much of the preparative work with very large high vacuum systems.
- (6) It is worth repeating that the idea that h.v.t. is inherently more time-consuming than dry-box techniques is a myth; with careful experimental planning, a greater degree of reproducibility and a lower level of impurities can be achieved by h.v.t. in a similar, if not shorter, time than that required for dry-box work. It is, however, true that it takes longer to master h.v.t. than to become familiar with dry-box techniques.
- (7) Finally, there are many operations, both preparative and investigative which *can* be done *without* h.v.t., but which are done *more efficiently*, *swiftly*, and *safely* by means of it.

1.2. Theoretical considerations

1.2.1. What is a vacuum?

The word vacuum in the English language is the same as the Latin word meaning a completely empty space. In practice, the word vacuum is used to describe any space in which the pressure is less than atmospheric pressure. Further, in order to specify the quality of a vacuum, various adjectives are used. Table 1.1. lists a selection of these terms, the associated pressure range, and the number of molecules per cubic centimetre that such a vacuum contains. It is clear that even the best known vacuum, in outer space, is not absolute. A knowledge of the amount of gas in a reaction volume at the operating pressure allows an assessment to be made of its possible effect on the reaction taking place.

Table 1.1. *Quality and nomenclature of vacua*

Pressure <i>p</i> /Torr	Number of molecules/cm ³ at 273 K	Quality of vacuum
760	2.73×10^{19}	
100	3.5×10^{18}	Coarse
~ 20	—	Water-pump vacuum
1	3.5×10^{16}	
10^{-3}	3.5×10^{13}	Fine
10^{-6}	3.5×10^{10}	High (usually the chemist's best)
10^{-10}	3.5×10^6	Ultra-high
10^{-16}	4	Outer space

Once a high vacuum system has actually been used for 'chemistry', i.e. has contained compounds other than the constituents of air, it is very difficult and tedious to evacuate it to below 10^{-5} Torr.

1.2.2. Units

The practical chemist working with vacuum systems has, in the past, used practical units, such as millimetres of mercury and atmospheres, for measuring the quality of the vacua which he has produced. However, for the modern chemist it is important to have a coherent system of units in which no numerical factors are inherent. Within the SI system, the unit of pressure is the pascal, which has the units and dimensions given below:

$$\text{Pa} = \text{m}^{-1} \text{kg s}^{-1}$$

Since many measuring devices and indeed many chemists still work with other units, it is useful to have the relations between all the units in common usage:

$$1 \text{ atm} = 760 \text{ Torr} = 760 \text{ mmHg} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ Pa}$$

In this work all pressures will be given in Torr.

1.2.3. General structure of a high vacuum system

Although the structure and components of high vacuum systems (h.v.s.) will be discussed in detail in Chapter 2, it is essential for an understanding of what follows to give here an outline of what is involved (see Fig. 2.1.).

Almost all the high vacuum systems with which we will be concerned have at one end a 'rough' pump, usually a rotary oil pump, capable of attaining *ca.* 10^{-3} Torr. This is followed by a high vacuum pump which can attain *ca.* 10^{-6} Torr, which is followed by a cold trap, the purpose of which is to condense out any volatile matter to prevent it entering, and possibly

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damaging, the pumps; and beyond this is the vacuum trunk line to which are attached the various reservoirs, measuring devices, reactors, etc., the evacuation of which is the purpose of the whole installation. Usually each of the components is separated from its neighbours by a tap or valve. Also, it is usually expedient to have a direct connection between the rough pump and the vacuum line so that this can be brought down to *ca.* 10^{-3} Torr before the high vacuum pump is engaged; this process is called 'roughing'.

1.2.4. Theory of pumping

In order to be able to design even the most elementary vacuum line, it is necessary to know something of the basic theory concerning the movement of molecules within the system. No attempt will be made here to instruct the reader in the details of vacuum physics and therefore the formulae given below have been kept simple. A more detailed discussion of the theory of gaseous flow can be found in Dushman's excellent review (Dushman, 1962). The object of the following discussion is simply to allow the reader to assess, without too much effort, the approximate efficiency of the system he is planning.

A chemist's vacuum line will often be pumped out several times within any working day and therefore the time taken to reach a useful vacuum should be as short as possible. The time taken by a system to reach the described vacuum depends upon the volume of the system, its internal surface area, the materials used for its construction, its cleanness, the speed of the pumps and the aerodynamic conductance of the system.

The conductance of any system depends on the nature of the gas flow; at higher pressures a viscous flow regime prevails and at lower pressures ($p < 10^{-1}$ Torr) a molecular flow regime. Turbulent flow, seldom considered when assessing the efficiency of a vacuum system, is encountered only when the pressure in the system is close to atmospheric pressure. As a general rule, if the efficiency of the system is adequate for the viscous flow regime then it will also be suitable for turbulent flow.

The change from a viscous to a molecular flow regime occurs when the mean free path \bar{L} of the gas molecules in the system exceeds the minimum physical dimensions of the system. The mean free path is a measure of the average distance a molecule travels between collisions. The derivation of \bar{L} involves a number of assumptions about the ideality of the gas and the nature of the collisions and by definition some 63.2% of the molecules in a particular gas collide with other molecules within the distance \bar{L} . The mean free path for any gas can be calculated from Equation (1.1)

$$\bar{L} = \kappa T / 2^{\frac{1}{2}} d^2 p \quad (1.1)$$

where κ is Boltzmann's constant, T the absolute temperature, d the effective diameter of the molecule, i.e. the distance between the centres of the two molecules at collision, and p is the pressure.