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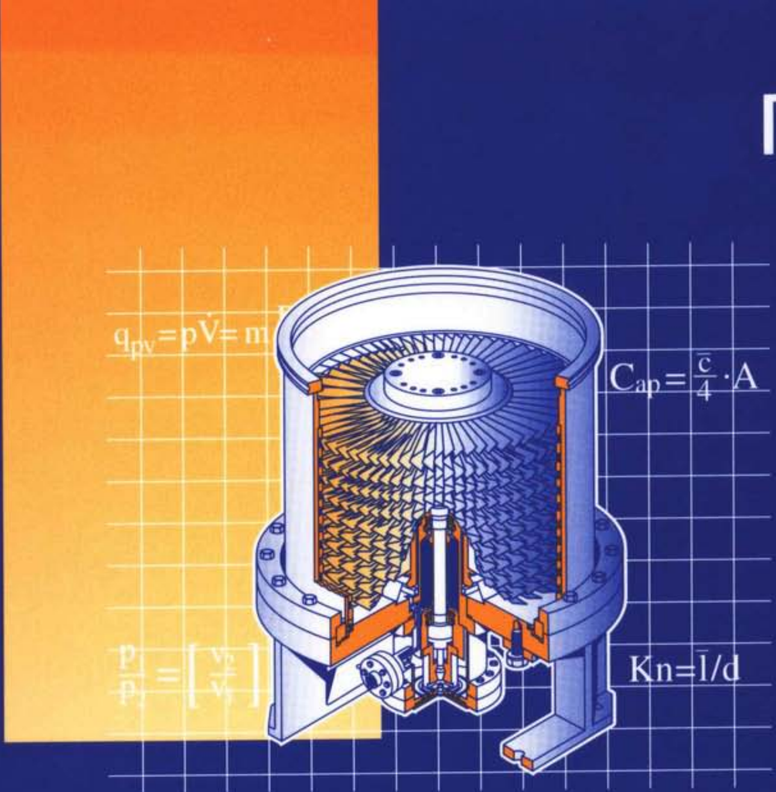

vacuum technology

calculations in chemistry

D. J. HUCKNALL *and* A. MORRIS

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Preface

In the preface to an earlier book on Vacuum Technology, one of us (DJH) pointed out that it would be a daunting task indeed to list all the activities and products to which vacuum technology makes a contribution. It is widely applied in the chemical sciences both in research and industry. Applications range from the efficient extraction of highly temperature-sensitive complex molecules to the creation of the conditions necessary to characterise surfaces unambiguously and to investigate surface phenomena. Many other areas, ranging from the study of short-lived atoms and free radicals to the design and deposition of 'smart' coatings on glass for solar control, could not have made significant progress without suitable vacuum systems.

In spite of the enormous use of vacuum processes, detailed knowledge of vacuum technology is often lacking. Design calculations are often attempted with incomplete or inadequately-interpreted data and, even with well-designed systems, operators may lack the confidence to use them optimally and often struggle to solve relatively small problems when they arise. In both cases, at some cost and delay, there is complete reliance on vacuum equipment manufacturers' appraisal.

This book has been written to assist and encourage both the newcomer and the experienced practitioner in vacuum technology. Problems in vacuum technology should be dealt with quantitatively and it is intended to be an accessible, applicable guide to how calculations in the subject are actually carried out. It is aimed at all those who use vacuum technology in chemical applications and who are involved in the design and operation of such equipment. It is aimed at users whether they be researchers or in industries as diverse as petro-chemical, pharmaceutical, nuclear, aerospace, environmental and semi-conductor. Although not specifically aimed at undergraduates, the authors hope that the first two chapters, particularly, will be of considerable use.

Vacuum technology takes necessary information from chemistry, physics and engineering. Possibly because of this, it is littered with a multiplicity of units, and both newcomers and experienced workers have often lacked the confidence to quantify their systems. It is fine to present clearly an equation in the text but it is quite a different matter to make use of it when one is not certain of what units to use or how to convert from one to another.

Although this book appears to be dominated by formulae, some of which seem complex, the reader should be reassured that no great demands are made. Obviously, some mathematical knowledge is required but, generally, it is only that which would normally have been acquired by anyone following a course in physical sciences or engineering.

The book is made up of seven chapters (plus additional, general material). The purpose of the first two is to remind the reader of information that is probably known already. This is essential if the best use is to be made of the information in later, topic-specific chapters. Throughout, numerous worked examples are given. An example usually illustrates material which immediately or closely precedes it. To the authors, they seem relevant and appropriate but others may disagree. What is important is that they are presented with detailed working and clearly-stated units (SI and SI-derived units have been preferred although in some cases, familiar and widely accepted units are used). They are there to build the reader's confidence and to encourage him to quantify his particular system.

In detail, Chapter 1 (Principles) reminds the reader that, in vacuum technology, gases and gas mixtures are, almost without exception, assumed to behave ideally. Information readily obtainable from the kinetic theory of gases (particle velocities, area-related flow *etc.*), of immense use to vacuum technologies, is also introduced.

Chapter 2 acknowledges the fact that in the design of vacuum systems, pump sets and pipework of an appropriate size must be used and that it is vital that the flow of gases into and out of the system be quantified. Terms widely used in vacuum technology are defined and the calculation of flow and related quantities under the three major types of gas flow is discussed.

The pump set on a vacuum system has to evacuate the system, starting from atmospheric pressure down to the required pressure, often in a given time. It must be able to maintain this pressure during operation of the vacuum process. Chapter 3 reviews the range of vacuum pumps available and the combinations that are used over the range from atmospheric pressure down to our current limits of measurement in the EHV range.

In Chapter 4, the gas sources and loads which are present in every vacuum system are considered. Since the gas loads from different sources have to be known or estimated to quantify the size of the pump set, their influence on attainable pressure is considered.

Chapter 5 considers the methods available for the measurement of both total and partial pressure in vacuum systems. For total pressure, the methods of measurement are described and, importantly, the uncertainty associated with that measurement is discussed. This may influence the choice of gauge. Also in Chapter 5, residual gas analysers (RGAs) for vacuum partial pressure measurements are described. These devices are being used increasingly for diagnostic work on vacuum systems.

Chapter 6 examines what, in the authors' opinion, are three important applications of vacuum technology in the chemical sciences. First, its use in chemical technology is clearly defined and, in many applications, the requirement for systems operating below 10^{-6} Pa is obvious. In both cases, typical systems are considered and quantified. The third topic concentrates on a technique (differential pumping) which is widely used in systems where high- and low-pressure areas must be interfaced. Specific systems are discussed to illustrate the usefulness of the technique.

A short concluding chapter (Chapter 7) summarises what has been presented and indicates future applications.

The book also includes a bibliography. Some of the works referred to are advanced texts on vacuum technology; others refer to sources of data from which tabulated information, given in the text, has been obtained.

Acknowledgements

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Contents

CHAPTER 1

Principles

1.1 INTRODUCTION

The purpose of this chapter is to state some of the basic ideas and assumptions that underpin vacuum technology.

To familiarise the reader with the scope of vacuum technology, it begins with a summary of the vacuum pressure range and typical applications in the chemical sciences.

The equation of state for a perfect gas is presented and expressions arising from this for pure gases and gas mixtures are given. The kinetic theory of gases, which is a useful model of perfect gases, is introduced and two particularly useful results are emphasised. These are the mean free path ($\bar{l}$) and the mean or thermal velocity ($\bar{c}$). Of particular importance is $\bar{c}/4$, which is numerically equal to the volume rate of flow per unit area and which can be used to determine quantities such as area-related pumping speeds, conductances, *etc.*

The transport properties, particularly viscosity and diffusion, of a perfect gas are discussed and the concepts of gas dynamics are briefly mentioned. Such methods can be applied to flowing gas in, for example, pipework or nozzles and jets.

1.2 SURVEY

Typical vacuum processes and plants can be classified according to the *pressure regions* in which they operate. These regions are shown overleaf.

1.3 PRESSURE

The term 'vacuum' is applied to pressures below, often considerably below, atmospheric pressure.

The object of vacuum technology is to reduce the number density of gas particles in a given volume of a system. At constant temperature, this

	Rough vacuum	*Medium vacuum*	*High vacuum*	*UHV–XHV*
Total pressure/mbar	10^3–1	1–10^{-3}	10^{-3}–10^{-7}	$<10^{-7}$–$<10^{-10}$
Typical applications				

Rough	Chemical technology (unit operations such as degassing, drying, filtration)
Medium	Chemical technology (distillation) Chemical Vapour Deposition (CVD) Sputtering processes
High	Physical Vapour Deposition (PVD) (coating of various substrates with a range of materials) GC-MS Kinetic studies
UHV–XHV	Surface science (*e.g.* AES, XPS, EELS) Fusion research Synchrotron radiation sources (various applications)

always corresponds to a reduction in gas pressure. The system pressure is just a convenient index of number density.

Pressure is the result of molecules, within a fluid, colliding with the walls of the containing vessel. Its magnitude depends on the force of the impacts exerted perpendicular to a defined area. The relationship between pressure (*p*), force (*F*) and area (*A*) is:

$$p = \frac{\mathrm{F}}{\mathrm{A}} \tag{1.1}$$

A force of 1 Newton (1 N = 1 kg.m $\mathrm{s^{-2}}$) on an area of 1 $\mathrm{m^2}$ exerts a pressure of 1 Pascal (Pa). Acceptable forms are kg.m $\mathrm{s^{-2}}$, kg m $\mathrm{s^{-2}}$, m kg $\mathrm{s^{-2}}$.

Other permissible pressure units are:

bar = 10^5 Pa
millibar (mbar) = 10^2 Pa

Although obsolete, the unit 'Torr' continues to be used. It is the pressure exerted by a mercury column of height 1 mm on the base area of the column at 0 °C.

$$1\ \text{torr} = 133.322\ \text{Pa} \cong 1.33\ \text{mbar}$$

Commonly used instruments, *e.g.* Pirani, capacitance diaphragm and ionisation gauges, for pressure measurement in vacuum systems indicate the *total* pressure. This is equal to the sum of the partial pressures of the individual components in a system. Unless otherwise stated, the term 'pressure' in vacuum technology invariably means total pressure.

The normal state of a gas is determined by the normal temperature (T_n) and normal pressure (p_n):

$$T_n = 0\,°\mathrm{C} = 273.15\,\mathrm{K}$$
$$p_n = 101325\,\mathrm{Pa} = 1013.25\,\mathrm{mbar}$$

p_n is also referred to as 'standard atmospheric pressure'. Atmospheric pressure is therefore regarded as approximately 1000 mbar.

1.4 IDEAL GAS LAW

With very few exceptions, gases and vapours at atmospheric pressure or below behave ideally. An ideal gas is one which obeys exactly the relationship:

$$pV = nRT \tag{1.2}$$

where p is the pressure, V the volume, n the amount of substance of the gas, T the absolute temperature and R, the gas constant, is a fundamental constant independent of the nature of the gas.

The amount of substance (n) has units of mol (or mole) or kmol (or kmole). It is related to the number of particles. One mol (or kmol) of a substance contains as many particles (atoms, molecules, ions, *etc.*) as there are atoms, in 12 g (or 12 kg) of ^{12}C. This is the Avogadro constant (N_A).

$$N_A = 6.022136 \times 10^{23}\,\mathrm{mol^{-1}} = 6.02213 \times 10^{26}\,\mathrm{kmol^{-1}}$$

If the mass of a substance is m and the molar mass of the substance is M, the amount of substance is:

$$n = \frac{m\,(\mathrm{g})}{M\,(\mathrm{g\,mol^{-1}})}\,\mathrm{mol} \tag{1.3}$$

The molar gas constant (R) has a value:

$$R = 8.3145472\,\mathrm{J\,K^{-1}\,mol^{-1}} = 8.3145472\,\mathrm{kJ\,K^{-1}\,kmol^{-1}}\,*$$

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* Source: CODATA Recommended Values of the Physical Constants, 1998, *J. Phys. Chem.*, Ref. Data, 1999, 28 (6).

In vacuum calculations, other units are often used:

$$\begin{aligned} R &= 83.14\,\mathrm{mbar\,L\,mol^{-1}\,K^{-1}} \\ &= 8.314 \times 10^4\,\mathrm{mbar\,L\,kmol^{-1}\,K^{-1}} \end{aligned}$$

Based on the above, the molar volume of a perfect gas at p_n and T_n is:

$$\begin{aligned} V_m &= \frac{RT_n}{p_n} \qquad (1.4) \\ &= \frac{83.145\,\mathrm{mbar\,L\,.mol^{-1}\,K^{-1}} \times 273.15\,\mathrm{K}}{1013.25\,\mathrm{mbar}} \\ &= 22.414\,\mathrm{L} \end{aligned}$$

The Boltzmann constant (k) is given by R/N_A. It has a value:

$$k = 1.380650 \times 10^{-23}\,\mathrm{J\,K^{-1}}$$

The particle number density (n) can be obtained from:

$$pV = \frac{N}{N_A}RT = NkT$$

$$p = \mathrm{nkT} \qquad (1.5)$$

where N is the number of particles under consideration. Under normal conditions:

$$\begin{aligned} \mathrm{n}_n &= \frac{p_n}{k\,T_n} = \frac{101325\,\mathrm{N\,m^{-2}}}{1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 273.15\,\mathrm{K}} \\ &= 2.6867 \times 10^{25}\,\mathrm{m^{-3}} \end{aligned}$$

At 293 K and p_n:

$$\begin{aligned} \mathrm{n}_{293\,\mathrm{K}} &= 2.51 \times 10^{25}\,\mathrm{m^{-3}} \\ &= 2.51 \times 10^{22}\,\mathrm{L^{-1}} \end{aligned}$$

At 293 K:

In 1 L at 1 mbar, there are 2.478×10^{19} particles
In 1 L at 10^{-6} mbar, there are 2.478×10^{13} particles
In 1 L at 10^{-10} mbar, there are 2.478×10^{9} particles

2.6867×10^{25} particles occupy 1 $\mathrm{m^3}$ at p_n and T_n.

1 mole of particles (6.022×10^{23}) occupies 22.414 L at p_n and T_n.

1.5 MIXTURES OF GASES: PARTIAL PRESSURES

If n mol of a gas (n_A) is injected into a volume (V), then the pressure (p_A) of A is given by:

$$p_A = n_A \left(\frac{RT}{V}\right) \tag{1.6}$$

If, instead of A, n mol of gas B (n_B) is injected into volume V, then the pressure (p_B) of B is given by:

$$p_B = n_B \left(\frac{RT}{V}\right)$$

If B was injected into V already containing A then, according to Dalton's law of partial pressures, the total pressure (p) is given by:

$$p = p_A + p_B = (n_A + n_B)\left(\frac{RT}{V}\right)$$

For several components (A, B, C, D, *etc.*):

$$p = p_A + p_B + p_C + p_D + \ldots$$

This law can also be expressed in terms of component *mole fractions*. The mole fraction (x) of a component is given by:

$$x_{\text{component}} = \frac{n_{\text{component}}}{n_{\text{total}}} \tag{1.7}$$

where n_{total} is the total number of moles in the system. Thus, in a mixture of gases (A, B, C, D, *etc.*) containing n_A, n_B, n_C, n_D *etc.*, the mole fraction of A is:

$$x_A = \frac{n_A}{n_{\text{total}}} \qquad (n_{\text{total}} = n_A + n_B + n_C + \ldots) \tag{1.8}$$

Therefore, the partial pressure of a component i in n mol of a perfect gas mixture with a total pressure p is:

$$p_i = n_i\left(\frac{RT}{V}\right) = x_i n\left(\frac{RT}{V}\right) = x_i p \tag{1.9}$$

Example 1.1

A 22.4 L vessel contains 2 mol H_2 and 1 mol N_2 at T_n. What are the mole fractions and the partial pressures of the components in the vessel?

Total no. of moles in vessel = 3

$$x_{H_2} = 2/3$$

$$x_{N_2} = 1/3$$

Since the molar volume (V_m) at p_n and T_n is 22.414 L then:

$$p_{H_2} = n_{H_2}\frac{RT}{V} = \frac{2\,\text{mol} \times 83.14\,\text{mbar L mol}^{-1}\,\text{K}^{-1} \times 273.15\,\text{K}}{22.414\,\text{L}}$$

$$= \underline{2026\,\text{mbar}}$$

Similarly, $$p_{N_2} = n_{N_2}\frac{RT}{V} = \underline{1013\,\text{mbar}}$$

$$\therefore \quad p = p_{H_2} + p_{N_2} = \underline{3039\,\text{mbar}}$$

Example 1.2

A 500 cm^3 vessel contains a H_2/N_2 mixture at 500 mbar and T_n. If the partial pressure of H_2 is 200 mbar what are the mole fractions of H_2 and N_2?

$$pV = nRT$$

$$n_{H_2} = \frac{200 \times 0.5\,\text{mbar L}}{83.14\,\text{mbar L mol}^{-1}\,\text{K}^{-1} \times 273\,\text{K}}$$

$$= 4.41 \times 10^{-3}\,\text{mol}$$

$$n_{N_2} = \frac{(500 - 200) \times 0.5\,\text{mbar L}}{83.14\,\text{mbar L mol}^{-1}\,\text{K}^{-1} \times 273\,\text{K}}$$

$$= 6.61 \times 10^{-3}\,\text{mol}$$

$$\therefore \quad n_{\text{total}} = 11.02 \times 10^{-3}\,\text{mol}$$

$$\therefore \quad \underline{x_{H_2} = 0.4}$$

and $$\underline{x_{N_2} = 0.6}$$

Example 1.3

4 L of methane has a pressure of 500 mbar at 20 °C. What is the mass of the gas?

$$pV = \frac{m}{M} RT$$

$$\therefore \quad m = \frac{500 \times 4\,\text{mbar L} \times 16\,\text{g mol}^{-1}}{83.14\,\text{mbar L mol}^{-1}\,\text{K}^{-1} \times 293\,\text{K}}$$

$$= \underline{1.31\,\text{g}}$$

Example 1.4

An excellent example of a gas mixture is atmospheric air. At sea level, the composition of dry air, in volume %, is approximately as follows:

N_2, 78.1; O_2, 20.9; Ar, 0.9; CO_2, 0.03; remainder 0.07.

What is the partial pressure of each when the total pressure is equal to p_n and the temperature is T_n? Calculate the mean molar mass of air.

Based on the above, 100 L of dry air contains approximately 78.1 L N_2, 20.9 L O_2, 0.9 L Ar, 0.03 L CO_2 and 0.07 L of traces of Kr, He, CH_4, *etc.*

At p_n, T_n, the molar volume of a perfect gas is 22.414 L mol^{-1}. The molar composition of 100 L of dry air is, therefore:

$$\begin{aligned}
&N_2 = 78.1/22.414 = 3.484\,\text{mol}\\
&O_2 = 20.9/22.414 = 0.933\,\text{mol}\\
&\text{Ar} = 0.9/22.414 = 0.040\,\text{mol}\\
&CO_2 = 0.00134\,\text{mol}\\
&\text{remainder} = 0.00312\,\text{mol}\\
\hline
&\text{Total no. of moles} = 4.4615\,\text{mol}
\end{aligned}$$

The corresponding mole fractions are:

$$x_{N_2} = 0.781;\ x_{O_2}; = 0.209\ x_{Ar} = 8.97 \times 10^{-3};\ x_{CO_2} = 3.00 \times 10^{-4}$$

The corresponding partial pressures at p_n are:

$$p_{N_2} = 0.781 \times 1013.25 = 791.4\,\text{mbar}$$

$$p_{O_2} = 0.209 \times 1013.25 = 211.8\,\text{mbar}$$

$$p_{Ar} = 8.97 \times 10^{-3} \times 1013.25 = 9.09\,\text{mbar}$$

$$p_{CO_2} = 3 \times 10^{-4} \times 1013.25 = 0.3\,\text{mbar}$$

Mean molar mass:

$$\overline{M} = \frac{m_{N_2} + m_{O_2} + m_{Ar} + m_{CO_2} + \ldots}{n_{\text{total}}}$$

$$m_{N_2} = 3.484\,\text{mol} \times 28\,\text{g}\,\text{mol}^{-1} = 97.55\,\text{g}$$

$$m_{O_2} = 0.933\,\text{mol} \times 32\,\text{g}\,\text{mol}^{-1} = 29.86\,\text{g}$$

$$m_{Ar} = 8.97 \times 10^{-3}\,\text{mol} \times 40\,\text{g}\,\text{mol}^{-1} = 0.359\,\text{g}$$

$$m_{CO_2} = 3.00 \times 10^{-4}\,\text{mol} \times 44\,\text{g}\,\text{mol}^{-1} = 0.0132\,\text{g}$$

$$\therefore\ \overline{M} = \frac{127.78\,\text{g}}{4.4615\,\text{mol}} = 28.6\,\text{g}\,\text{mol}^{-1}$$

$$\underline{\sim 29\,\text{g}\,\text{mol}^{-1}}$$

1.6 KINETIC THEORY OF GASES

A very useful model for the behaviour of an ideal gas is as follows:

- In a volume V, there are N particles of mass m.
- Each particle has a velocity $\vec{c}$ (strictly, this is a vector with components c_x, c_y and c_z).
- Values of c cover the complete range between 0 and ∞.
- Particles can be regarded as point masses which exert no force on each other beyond a separation distance $r > R$ (R is known as the interactive radius). At $r < R$ there is an infinite repulsive force between the particles involved. They therefore behave like perfectly elastic spheres of radius $R/2$.
- On impact with each other, the velocities of the partners change in both value and direction.
- Particles colliding with the container walls are elastically reflected, creating gas pressure (p).

Because they undergo frequent collisions, particles will not have a constant velocity or move in specific directions such as the x-, y- or z-direction. The Maxwell–Boltzmann frequency distribution is used to describe the non-uniform distribution of particle velocities (c) brought about by collisions.

From the Maxwell–Boltzmann distribution, various velocities may be defined. These are:

The most probable velocity $(c_p) = \sqrt{\frac{2RT}{M}}\,\text{m}\,\text{s}^{-1}$ (1.10)

The mean velocity or thermal velocity $(c_{av}, \overline{c}) = \sqrt{\frac{8RT}{\pi M}}\,\text{m}\,\text{s}^{-1}$ (1.11)

The root mean square velocity (rms) or effective velocity $(c_{eff}) = \sqrt{\frac{3RT}{M}}\,\text{m}\,\text{s}^{-1}$ (1.12)

A particularly useful quantity in the case of a Maxwell distribution is:

$$\text{Mean x-component of velocity} = \frac{\bar{c}}{4} \tag{1.13}$$

$$= \sqrt{\frac{RT}{2\pi M}}\,\mathrm{m\,s^{-1}} \tag{1.14}$$

$$= 36.38\sqrt{\frac{T}{M}}\,\mathrm{m\,s^{-1}} \tag{1.15}$$

$\bar{c}/4$ is equal to the mean normal component of velocity relative to any reference surface. It is numerically equal to the maximum area-related pumping speed (volume rate of flow per unit area) of an ideal pump for a gas at temperature T.

Example 1.5

Calculate the mean velocity of Ar atoms at 20 °C.

$$\bar{c} = \sqrt{\frac{8 \times 8.314 \times 10^3\,\mathrm{J\,kmol^{-1}\,K^{-1}} \times 293\,\mathrm{K}}{\pi \times 39.95\,\mathrm{kg\,kmol^{-1}}}}$$

$$\underline{= 394.0\,\mathrm{m\,s^{-1}}}$$

Example 1.6

The interior of a spherical vessel of radius $r = 0.5\,\mathrm{m}$ is covered with a monomolecular layer of gas particles each having a cross-sectional area $(A_{\mathrm{part}}) = 10^{-19}\,\mathrm{m^2}$.

What would be the pressure increase if all the particles were desorbed at a temperature of 300 °C?

Pressure increase (Δp) is given by:

$$\Delta p = \Delta n kT = \frac{N}{V}kT$$

where Δn = the number of particles in the gas phase after desorption.

$$N = A/A_{\mathrm{part}} \text{ where } A = \text{surface area of vessel}$$
$$= 4\pi r^2/10^{-19}\text{particles}$$

$$\frac{N}{V} = \frac{4\pi r^2 \times 10^{19}}{4\pi r^3/3} = \frac{3 \times 10^{19}}{r}$$

$$\therefore\quad \Delta p = \frac{3 \times 10^{19} \times 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 573.15\,\mathrm{K}}{0.5\,\mathrm{m}}$$

$$= \frac{3 \times 1.38 \times 10^{-4}\,\mathrm{J\,K^{-1}} \times 573.15\,\mathrm{K}}{0.5\,\mathrm{m}}$$

$$\underline{= 4.7 \times 10^{-1}\,\mathrm{N\,m^{-2}} = 0.47\,\mathrm{Pa} = 4.7 \times 10^{-3}\,\mathrm{mbar}}$$

Example 1.7

Calculate the effective speed of
(i) N_2 molecules at 1600 °C.
(ii) H_2 molecules at 4K.

(i)

$$c_{\mathrm{eff}} = \sqrt{3RT/M}\,\mathrm{m\,s^{-1}}$$

$$= \sqrt{\frac{3 \times 8.314 \times 10^3\,\mathrm{J\,mol^{-1}\,K^{-1}} \times 1873.15\,\mathrm{K}}{28\,\mathrm{kg\,kmol^{-1}}}}$$

$$\underline{= 1292\,\mathrm{m\,s^{-1}}}$$

(ii)

$$c_{\mathrm{eff}} = \sqrt{\frac{3 \times 8.314 \times 10^3\,\mathrm{J\,kmol^{-1}\,K^{-1}} \times 4\,\mathrm{K}}{2\,\mathrm{kg\,kmol^{-1}}}}$$

$$\underline{= 223\,\mathrm{m\,s^{-1}}}$$

Example 1.8

At what temperature would:
(i) Ar atoms have a mean velocity ($\bar{c}$) = 500 m s^{-1}?
(ii) ^{4}He atoms have a mean velocity of 150 m s^{-1}?

(i)

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}\,\mathrm{m\,s^{-1}}$$

$$\therefore \quad 500\,\mathrm{m\,s^{-1}} = \sqrt{\frac{8 \times 8.314 \times 10^3\,\mathrm{J\,kmol^{-1}\,K^{-1}} \times T}{\pi \times 40\,\mathrm{kg\,k\,mol^{-1}}}}$$

$$\therefore \quad T = \frac{(500)^2\,\mathrm{m^2\,s^{-2}} \times \pi \times 40\,\mathrm{kg\,kmol^{-1}}}{8 \times 8.314 \times 10^3\,\mathrm{J\,kmol^{-1}\,K^{-1}}}$$

$$\underline{= 472\,\mathrm{K}\ (\sim 199\,^{\circ}\mathrm{C})}$$

(ii)

$$\bar{c} = \sqrt{\frac{8RT}{\pi \mathrm{M}}}\,\mathrm{m\,s^{-1}}$$

$$\therefore \quad 150\,\mathrm{m\,s^{-1}} = \sqrt{\frac{8 \times 8.314 \times 10^3\,\mathrm{J\,kmol^{-1}\,K^{-1}} \times T}{\pi \times 4\,\mathrm{kg\,kmol^{-1}}}}$$

$$\therefore \quad T = \frac{(150)^2\,\mathrm{m^2\,s^{-2}} \times \pi \times 4\,\mathrm{kg\,kmol^{-1}}}{8 \times 8.314 \times 10^3\,\mathrm{J\,kmol^{-1}\,K^{-1}}}$$

$$\underline{= 4.3\,\mathrm{K}}$$

Wall flux density (area-related collision rate). A measure of the rate of flow of matter from one part of a system to another is given by the *flux* (flow rate per unit area). For the transportation of matter, this is given by:

$$j_N = \frac{n\bar{c}}{4} \tag{1.16}$$

where n is particle number density ($n = pkT = N/V$), N is number of particles and $\bar{c}/4$ is mean normal component of velocity (mean or thermal speed of the gas in the x-direction).

Effusion of material from a hole. If a gas is present in a container but that container has a small hole leading to a low-pressure region, the gas will flow through the hole until the pressure is equal on both sides. This process is termed effusion.

If the wall has a hole of area ΔA, then the particle throughput (s^{-1}) would be:

$$\Delta q_N = \frac{n\bar{c}}{4} \cdot \Delta A = \left(\frac{p\bar{c}}{4kT}\right)\Delta A$$

This is applicable if there are no interparticle collisions, *i.e.* if the mean free path is no smaller than the dimensions of the aperture or slit.

The volume rate of flow (Δq_V) = volume/time can be obtained:

$$V = \frac{N}{n}$$

$$\therefore \quad \frac{\Delta V}{\Delta t} = \frac{\Delta N}{\Delta t}\frac{1}{n} = \frac{\Delta q_N}{n}$$

$$\therefore \quad \text{Volume rate of flow } = \frac{\bar{c}}{4}\Delta A \tag{1.17}$$

Surface-related condensation rate. This is proportional to the number of molecules incident on a surface

$$j_N = s_{\text{cond}} \frac{n\bar{c}}{4} \tag{1.18}$$

where s_{cond} = surface condensation coefficient

$$= \frac{\text{no. of particles condensed}}{\text{no. of incident particles}}$$

At sufficiently low gas and surface temperatures, values of $s_{\mathrm{cond}} = 1$ can be assumed and Equation 1.17 applied.

Example 1.9

A high vacuum chamber contains a liquid N_2-cooled surface (A= 400 cm^2) to provide a high, *in situ*, pumping speed for water molecules desorbing from its surface. Calculate the pumping speed for water vapour at 50 °C if all the impinging molecules are trapped.

$$\text{Mean normal component of velocity} = \bar{c}/4\ \mathrm{m\,s^{-1}}$$

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}\ \mathrm{m\,s^{-1}} = 145.5\sqrt{\frac{T}{M}}\ \mathrm{m\,s^{-1}}$$

$$\therefore\quad \bar{c}_{\mathrm{H_2O,50\,^\circ C}} = 616\ \mathrm{m\,s^{-1}}$$

Maximum area-related pumping speed per 1 m^2

$$= \frac{\bar{c}}{4}\ \mathrm{m\,s^{-1}} \times 1\ \mathrm{m^2} = 154\ \mathrm{m^3\,s^{-1}}$$

$$= 154 \times 10^3\ \mathrm{L\,s^{-1}}$$

$$\therefore\quad S/\mathrm{cm^2} = 15.4\ \mathrm{L\,s^{-1}}$$

$$S_{400\,\mathrm{cm^2}} = \underline{6160\ \mathrm{L\,s^{-1}}}$$

Example 1.10

A Knudsen cell was used to determine the vapour pressure of germanium (M= 72.6 g mol^{-1}) at 1000 °C. A mass of 4.3×10^{-5} g was lost through a hole of radius 0.5 mm in 2 h. What is the vapour pressure of Ge?

Assuming that Ge vapour behaves ideally, then:

$$p\dot{V} = \frac{\dot{m}}{M}RT = q_{pV}\ \text{(the } pV \text{ throughput)}$$

where $\dot{V}$ is the volume flow rate through the hole and $\dot{m}$ is the mass flow of Ge through the hole.

$$\dot{m} = \frac{4.3 \times 10^{-5}}{2 \times 3600}\ \mathrm{g\,s^{-1}} = 5.97 \times 10^{-9}\ \mathrm{g\,s^{-1}}$$

$$= \frac{p\dot{V} \times M}{RT}$$

$$\therefore\quad p\dot{V} = \frac{5.97 \times 10^{-9}\ \mathrm{g\,s^{-1}} \times 83.14\ \mathrm{mbar\,L\,mol^{-1}\,K^{-1}} \times 1273\ \mathrm{K}}{72.6\ \mathrm{g\,mol^{-1}}}$$

$$= 8.71 \times 10^{-6}\ \mathrm{mbar\,L\,s^{-1}}$$

$$\dot{V} = \frac{\bar{c}}{4}\Delta A$$

where $\bar{c}$ = mean velocity = $145.5\sqrt{T/M}$

ΔA = area of the hole

$$\therefore \quad \dot{V} = \frac{609.2\,\mathrm{m\,s^{-1}} \times \pi(5 \times 10^{-4})^2\,\mathrm{m}^2}{4}$$

$$= 1.196 \times 10^{-4}\,\mathrm{m^3\,s^{-1}}$$
$$= 0.1196\,\mathrm{L\,s^{-1}}$$

$$\therefore \quad 0.1196\,\mathrm{L\,s^{-1}} \times p_{\mathrm{Ge}}\,\mathrm{mbar} = 8.71 \times 10^{-6}\,\mathrm{mbar\,L\,s^{-1}}$$

$$\therefore \quad p_{\mathrm{Ge}} = \frac{8.7 \times 10^{-6}}{0.1196}\,\mathrm{mbar}$$

$$\underline{= 7.3 \times 10^{-5}\,\mathrm{mbar}}$$

Mean free path ($\bar{l}$). With the large number of gas particles present in a volume of gas at a given pressure, a large number of collisions can occur. Calculation of the collision frequency allows the mean free path ($\bar{l}$) of the particles to be determined. This is the average distance travelled by a particle between collisions.

A simple treatment is to regard colliding particles as hard spheres and a collision to occur whenever the centres of two molecules come within some distance (d) of each other. With a moving particle a collision area called the collision cross-section (σ) is generated, where σ is equal to πd^2 if d is the particle diameter. Some examples of collision cross-sections are given in Table 1.1. If colliding particles are travelling with an average *relative* speed $\sqrt{2}\,\bar{c}$, then the number of collisions a *single* particle makes per second is:

$$z = \sqrt{2}\bar{c}n\sigma \tag{1.19}$$

where n is the particle number density. From this, an expression for $\bar{l}$ ($= \bar{c}/z$) can be derived:

$$\bar{l} = \frac{1}{\sqrt{2}n\sigma}$$

and, for a single gas:

$$\bar{l} = \frac{1}{\sqrt{2}n\pi d^2} \tag{1.20}$$

Here $d = 2r$, where r is the radius of the colliding particles. For two different particles in a gas mixture $d = r_1 + r_2$. d is sometimes called the collision radius (R_∞) to denote an 'active' sphere of radius R_∞ and active cross-section $\pi R^2{}_\infty$.

Table 1.1 *Collision cross-sections*

Gas	*σ/nm²*
He	0.21
Ar	0.36
H_2	0.27
N_2	0.43
O_2	0.40
CO_2	0.52

Example 1.11

If the collision cross-section of N_2 is $0.43 \times 10^{-18}\,\mathrm{m}^2$, what is the collision cross-sectional radius ($d = 2r$)?

$$\sigma = \pi d^2$$

$$\therefore \quad d = \sqrt{\sigma/\pi} = \sqrt{(0.43 \times 10^{-18})\mathrm{m}^2/\pi}$$

$$= 0.37 \times 10^{-9} m$$

$$\underline{= 3.7 \times 10^{-10} m}$$

The particle number density (n) $= p/kT$, hence:

$$\bar{l} = \frac{kT}{\sqrt{2}p\pi\, d^2}$$

and

$$\bar{l}p = \frac{kT}{\sqrt{2}\pi d^2} = \frac{RT}{\sqrt{2}\pi N_A d^2} \qquad (1.21)$$

Note that the expression $\bar{l}p$ is a convenient way of stating the variation of $\bar{l}$ with p for various gases and is commonly presented in tabular form (see Table 1.2).

Table 1.2 *Values of $\bar{l}p$ for a range of gases; $T = 293$ K*

Gas	*$\bar{l}p$ (mmbar) ($\times 10^5$) ref. (a)**
N_2	6.4
Air	6.5
O_2	6.5
He	19
H_2	12.2
Ar	6.8

*Throughout, several sources of data are repeatedly cited as refs. (a, b, c *etc.*). Details of these are given in the Bibliography on page 224.

Example 1.12

Calculate the $\bar{l}p$ value for N_2 at 20 °C.

$$\bar{l}p = \frac{RT}{\sqrt{2}\,\pi N_A R_\infty^2}$$

From Example 1.11, R_∞ $(= d) = 3.7 \times 10^{-10}$ m.

$$\therefore \quad \bar{l}p = \frac{8.314 \times 10^3\,\text{Pa m}^3\,\text{kmol}^{-1}\,\text{K}^{-1} \times 293\,\text{K}}{\sqrt{2}\,\pi \times 6.022 \times 10^{26}\,\text{kmol}^{-1} \times (3.7 \times 10^{-10})^2\,\text{m}^2}$$

$$= \frac{2.44 \times 10^6\,\text{Pa m}^3\,\text{kmol}^{-1}}{3.66 \times 10^2 \times 10^6\,\text{kmol}^{-1}\,\text{m}^2}$$

$$= 6.67 \times 10^{-3}\,\text{Pa m}$$
$$\underline{= 6.67 \times 10^{-5}\,\text{m mbar}}$$

Example 1.13

If He has a collision cross-section radius of 2.18×10^{-10} m, calculate the mean free path of He atoms at 10^{-4} mbar and 293 K.

$$\bar{l}p = \frac{8.314 \times 10^3\,\text{Pa m}^3\,\text{kmol}^{-1}\,\text{K}^{-1} \times 293\,\text{K}}{\sqrt{2}\,\pi \times 6.022 \times 10^{26}\,\text{kmol}^{-1} \times (2.18 \times 10^{-10})^2\,\text{m}^2}$$

$$= 19.2 \times 10^{-5}\,\text{m mbar}$$
$$= 19.2 \times 10^{-3}\,\text{cm mbar}$$

$$\therefore \quad \bar{l}_{\text{He},293\,\text{K}} \ \underline{= 192\,\text{cm at } 10^{-4}\,\text{mbar}}$$

The expression given above in Equation (1.19):

$$z = \sqrt{2}\,\bar{c}\,\mathrm{n}\,\sigma = \sqrt{2}\,\bar{c}\,\sigma\,\frac{p}{kT}$$

refers to the number of collisions made by a single particle per unit time.

If the total number of interparticle collisions is required, per unit volume per unit time, this expression is divided by 2 (because x. . . . . x^1 and x^1. . . . .x are counted as only one collision) and multiplied by *n*:

$$z_{\mathrm{x-x}} = \tfrac{1}{2}zn \qquad (1.22)$$

$$= \tfrac{1}{2}z\frac{p}{kT}$$

Example 1.14

Calculate the number of collisions per unit volume per unit time between oxygen molecules in air at 25 °C and 1 bar. Assume the radius of oxygen molecules is 1.78×10^{-10} m.

The collision number (z) for a single O_2 molecule:

$$z = \sqrt{2}\,\bar{c}\,n\,\sigma = \frac{\sqrt{2}\,\bar{c}\,p\,\sigma}{kT}$$

$$\sigma = \pi d^2;\ d_{\mathrm{O_2}} = 2r_{\mathrm{O_2}} = 2 \times 1.78 \times 10^{-10}\,\mathrm{m}$$
$$= 3.56 \times 10^{-10}\,\mathrm{m}$$

$$d^2 = 1.27 \times 10^{-19}\,\mathrm{m}^2$$

$$\therefore\ \sigma = 3.98 \times 10^{-19}\,\mathrm{m}^2$$

$\bar{c} = 145.5\sqrt{T/\mathrm{M}}$ where $T = 298$ K and $\mathrm{M} = 32\,\mathrm{g\,mol^{-1}}$
$= 444\,\mathrm{m\,s^{-1}}$

From Example 1.4:

$$p_{\mathrm{O_2}} = 209.5\,\mathrm{mbar}\ \text{(in 1 bar atmospheric air)}$$
$$= 20950\,\mathrm{Pa}$$

$$\therefore\quad z = \frac{\sqrt{2} \times 3.98 \times 10^{-19}\,\mathrm{m}^2 \times 444\,\mathrm{m\,s^{-1}} \times 2.095 \times 10^4\,\mathrm{N\,m^{-2}}}{1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 298\,\mathrm{K}}$$

(Note 1 J = 1 N m)

$$= \frac{5.238 \times 10^{-12}\,\mathrm{m^3\,s^{-1}\,N\,m^{-2}}}{1.3807 \times 10^{-23}\,\mathrm{N\,m} \times 298}$$

$$\underline{= 1.273 \times 10^{9}\,\mathrm{s^{-1}}}$$

$$z_{O_2-O_2} = \tfrac{1}{2} z \frac{p}{kT}$$

$$= \tfrac{1}{2} \times \frac{1.273 \times 10^{9}\,\mathrm{s^{-1}} \times 20950\,\mathrm{N\,m^{-2}}}{1.3807 \times 10^{-23}\,\mathrm{N\,m\,K^{-1}} \times 298\,\mathrm{K}}$$

$$= 3.24 \times 10^{33}\,\mathrm{s^{-1}\,m^{-3}}$$

$$= \underline{3.24 \times 10^{27}\,\mathrm{s^{-1}\,cm^{-3}}}$$

Example 1.15

A system at 230 K contains 5×10^{18} N_2 molecules per m^3. Calculate the mean free path if $\sigma_{N_2} \sim 0.43\,\mathrm{nm}^2$.

$$n = \frac{p}{kT}$$

$$\therefore \quad p = 5 \times 10^{18}\,\mathrm{m^{-3}} \times 1.38 \times 10^{-23}\,\mathrm{N\,m\,K^{-1}} \times 230\,\mathrm{K}$$

$$= 1.59 \times 10^{-2}\,\mathrm{N\,m^{-2}}$$

$$= 1.59 \times 10^{-4}\,\mathrm{mbar}$$

$$\bar{l} = \frac{kT}{\sqrt{2} p \sigma_{N_2}}$$

$$= \frac{1.38 \times 10^{-23}\,\mathrm{N\,m\,K^{-1}} \times 230\,\mathrm{K}}{\sqrt{2} \times 1.59 \times 10^{-2}\,\mathrm{N\,m^{-2}} \times 0.43 \times 10^{-18}\,\mathrm{m^2}}$$

$$= 0.33\,\mathrm{m}$$

$$= \underline{33\,\mathrm{cm}}$$

1.7 TRANSPORT PROPERTIES

The flow of material from one region to another is an example of a transport process. Transport processes frequently occur in low-pressure systems and may involve:

mass transfer *e.g.* diffusion, effusion
energy transfer *e.g.* thermal conductivity
momentum transfer *e.g.* viscosity.

1.7.1 Diffusion

Diffusion flux (j_{diff}) (the amount of material passing through unit area in unit time) is proportional to the number density gradient:

$$j_{\text{diff}} = -D \operatorname{grad} n \tag{1.23}$$

$$\text{i.e.}\quad j_{\mathrm{diff},x} \propto \mathrm{d}n/\mathrm{d}x$$

$$= -D\frac{\mathrm{d}n}{\mathrm{d}x}$$

The subscript for the flux denotes that the flow of material along the x-axis is proportional to the gradient along that axis.

The diffusion coefficient D is given by:

$$D = \bar{l}\,\frac{\bar{c}}{3} \tag{1.24}$$

Example 1.16

Calculate the diffusion coefficient for He in air at 1 mbar at 20 °C.

$$\bar{l}p_{\mathrm{air}} = 6.5 \times 10^{-5}\ \mathrm{m\,mbar}\ \text{(see Table 1.2)}$$

$$\therefore\quad \bar{l}_{\mathrm{air,1\,mbar}} = 6.5 \times 10^{-5}\ \mathrm{m}$$

$$\bar{c}_{\mathrm{He,293\,K}} = 145.5\sqrt{\frac{T}{M}}\ \mathrm{m\,s^{-1}}$$

$$= 1245\ \mathrm{m\,s^{-1}}$$

$$\therefore\quad D = \frac{\bar{l}\bar{c}}{3} = \underline{0.027\ \mathrm{m^2\,s^{-1}}}$$

As the mean free path decreases with increasing pressure and the mean speed increases with increasing temperature, D will vary accordingly.

Example 1.17

Calculate the diffusion coefficient for argon at 25 °C and a pressure of (a) 1×10^{-3} mbar and (b) at 1000 mbar. If a pressure gradient of 0.1 atm cm^{-1} is established in a pipe containing Ar, what is the flow of gas due to diffusion?

$$(\sigma_{\mathrm{Ar}} = 0.36\ \mathrm{nm^2})$$

$$D = \frac{\bar{l}\bar{c}}{3}\ \mathrm{m^2\,s^{-1}}$$

$$\bar{l} = \frac{kT}{\sqrt{2}\,\sigma p m}$$

(a)

$$\bar{l} = \frac{1.381 \times 10^{-23}\ \mathrm{N\,m\,K^{-1}} \times 298\ \mathrm{K}}{\sqrt{2} \times (0.36 \times 10^{-18})\ \mathrm{m^2} \times 0.1\ \mathrm{N\,m^{-2}}}$$

$$= \frac{4.12 \times 10^{-21}\,\mathrm{N\,m}}{5.1 \times 10^{-20}\,\mathrm{N}}$$

$$\underline{= 8.1 \times 10^{-2}\mathrm{m}}$$

$$\bar{c} = 145.5\sqrt{\frac{T}{M}}\,\mathrm{m\,s^{-1}}$$

So for Ar at 298 K:

$$\bar{c} = 397\,\mathrm{m\,s^{-1}}$$

$$\therefore\ D = \frac{\bar{l}\bar{c}}{3} = \frac{8.1 \times 10^{-2}\,\mathrm{m} \times 397\,\mathrm{m\,s^{-1}}}{3}$$

$$= 10.7\,\mathrm{m^2\,s^{-1}}$$

$$j_{\mathrm{diff}} = -D \times -(\mathrm{d(mols)}/\mathrm{d}x)$$

where x is the direction of the length of the pipe.

$$\therefore\ j_{\mathrm{diff}} = -10.7 \times 10^4\,\mathrm{cm^2\,s^{-1}} \times -\frac{\mathrm{d(mols)}}{\mathrm{d}x}$$

$$\text{where}\quad \frac{-\mathrm{d(mols)}}{\mathrm{d}x} = 0.1\ \mathrm{atm\,cm^{-1}}$$

Given that 1 mol of an ideal gas occupies 24.46 L at 298 K and 101325 Pa, then 24.46 L at 298 K and 0.1 atm contain 1 × 0.1 mol.

$$\therefore\ \frac{-\mathrm{d(mol)}}{\mathrm{d}x} = \frac{0.1\,\mathrm{mol}}{24.46 \times 10^3\,\mathrm{cm^3} \times 1\,\mathrm{cm}}$$

$$= 4.09 \times 10^{-6}\,\mathrm{mol\,cm^{-4}}$$

$$\therefore\ j_{\mathrm{diff}} = 10.7 \times 10^4\,\mathrm{cm^2\,s^{-1}} \times 4.09 \times 10^{-6}\,\mathrm{mol\,cm^{-4}}$$

$$\underline{= 0.44\,\mathrm{mol\,cm^{-2}\,s^{-1}}}$$

(b) At 1000 mbar

$$\bar{l} = 8.1 \times 10^{-8}\,\mathrm{m}$$

$$\bar{c} = 397\,\mathrm{m\,s^{-1}}$$

$$\therefore\ D = 1.07 \times 10^{-8}\mathrm{m^2 s^{-1}}$$

$$j_{\mathrm{diff}}\ \underline{= 4.4 \times 10^{-7}\,\mathrm{mol\,cm^{-2}\,s^{-1}}}$$

1.7.2 Viscosity (Internal Friction in Gases)

If a fluid such as air flows over a flat plate placed with its surface parallel to the stream, particles in the vicinity of the surface are slowed down by viscous forces. Fluid particles adjacent to the surface stick to it and have zero velocity relative to the boundary. Other fluid particles are retarded as a result of sliding over the immobilised particles. The effects of viscous forces originating at the boundary extend for a certain distance (δ, the boundary layer thickness). The effects of viscous forces originating at the boundary are not extensive and the velocity soon approaches free stream velocity.

When a fluid, with a uniform velocity, enters a tube, a boundary layer gradually builds up until it reaches the centre of the tube. The velocity profile is then said to be fully developed and may be assumed not to vary down the tube. In laminar flow it is developed at a distance l from the entrance where:

$$\frac{l}{D_\mathrm{h}} = 0.0288 Re \tag{1.25}$$

In Equation (1.25) l is the entrance or approach length, D_h is hydraulic diameter (see below) and Re is the Reynolds number.

$$\therefore \quad l = 0.0288 Re\, D_\mathrm{h}$$

$D_\mathrm{h} = 4\,A/B$, where A is the area and B is the perimeter. For a tube of circular cross-section, D_h = tube diameter.

The Reynolds number is given by:

$$Re = \frac{\rho\, v_\mathrm{m}\, D_\mathrm{h}}{\eta} \tag{1.26}$$

where ρ is the fluid density, v_m is the (mean) stream velocity, D_h is the hydraulic diameter and η is the dynamic viscosity. In long ducts, the flow is laminar when $Re < 2100$. There is a transition to turbulent flow at higher Re ($2100 < Re < 10^4$) and turbulence beyond.

For gases at high pressure $\bar{l} \ll d$, where d is a critical length in the gas flow, *e.g.* the diameter of a tube, flow channel, *etc.*, the expression for viscosity is:

$$\eta = \frac{4}{\pi \bar{c}} \bar{l} p \tag{1.27}$$

At high pressures, experimental results indicate that the dynamic viscosity of gases is independent of pressure over a wide range (approximately 1 mbar to 50 bar). Table 1.3 lists some values for the dynamic viscosity of gases.

Table 1.3 *Dynamic viscosity (η) of gases at* T *(K)*

Gas	η ($\times 10^6$) $kg\,m^{-1}\,s^{-1}$ ($\equiv Pa\,s$) 293 K (ref. b)	300 K (ref. c)
H_2	8.8	9.0
He	19.6	20.0
H_2O	—	10.0
N_2	17.6	17.9
Air	18.2	—
O_2	20.4	20.8
Ar	22.3	22.9

Example 1.18

Calculate the dynamic viscosity of helium at 25 °C.

$$\eta = \frac{4}{\pi \bar{c}} \bar{l}p$$

Values for $\bar{l}p$ for various gases at 20 °C can be found in Table 1.2 or can be calculated from:

$$\bar{l}p = \frac{RT}{\sqrt{2}\,\pi N_A d^2}$$

where d is the collision radius (= 2.18×10^{-10} m for He (see Example 1.13)).

$$\bar{l}p_{\mathrm{He,25\,°C}} = \frac{8.314 \times 10^3\ \mathrm{Pa\,m^3\,kmol^{-1}\,K^{-1}} \times 298\ \mathrm{K}}{\sqrt{2} \cdot \pi \times 6.022 \times 10^{26}\ \mathrm{kmol^{-1}} \times (2.18 \times 10^{-10})^2\ \mathrm{m^2}}$$

$$= 1.95 \times 10^{-2}\ \mathrm{Pa\,m}$$
$$= 1.95 \times 10^{-4}\ \mathrm{mbar\,m}$$

$$\eta_{\mathrm{He,25\,°C}} = \frac{4 \times 1.95 \times 10^{-2}\ \mathrm{Pa\,m}}{\pi \times \bar{c}_{\mathrm{He,\,25\,°C}}}$$

$$\bar{c}_{\mathrm{He,25\,°C}} = 145.5\sqrt{T/M} = 1256\ \mathrm{ms^{-1}}$$

$$\eta_{\text{He, }25\,°\text{C}} = \frac{4 \times 1.95 \times 10^{-2}\,\text{Pa m}}{\pi \times 1256\,\text{m s}^{-1}}$$

$$\begin{aligned}\eta_{\text{He,}25\,°\text{C}} &= 1.98 \times 10^{-5}\,\text{Pa s}\\ &= \underline{1.98 \times 10^{-5}\,\text{kg m s}^{-1}} \text{ since } 1\,\text{N} = 1\,\text{kg m s}^{-2}\end{aligned}$$

Example 1.19

H_2 has a dynamic viscosity of 0.908×10^{-5} Pa s at 25 °C. Calculate its $\bar{l}p$ value.

$$\eta_{H_2,25\,°\text{C}} = \frac{4}{\pi\bar{c}}(\bar{l}p)$$

$$\begin{aligned}\bar{c}_{H_2,25\,°\text{C}} &= 145.5\sqrt{298/2}\,\text{m s}^{-1}\\ &= 1776\,\text{m s}^{-1}\end{aligned}$$

$$\begin{aligned}\therefore\quad (\bar{l}p) &= \frac{\eta_{H_2}\pi\bar{c}}{4}\\ &= 1.267 \times 10^{-2}\,\text{Pa m}\\ &= 1.267 \times 10^{-4}\,\text{mbar m}\end{aligned}$$

The nature of gas flow in pipes, ducts, *etc.* changes with gas pressure. The type of flow is defined by the Knudsen number (*Kn*):

$$Kn = \bar{l}/d \tag{1.28}$$

where d is some characteristic dimension of the system, *e.g.* pipe diameter, and $\bar{l}$ is the mean free path of the gas.

Gas flow is generally divided into three types (see Table 1.4) defined by the Knudsen number. In continuum flow, whether laminar or turbulent conditions prevail depends on the Reynolds number.

Table 1.4 *The dependence of flow type on Kn*

Kn values	*Flow type*
$Kn < 0.01$	Viscous (continuum)
$Re < 2300$	laminar
$Re > \sim 4000$	turbulent
$0.01 < Kn < 0.5$	Transitional (Knudsen)
$Kn > 0.5$	Molecular

Re can also be written in terms of gas throughput. For a tube of circular cross-section, diameter *d*:

$$Re = \frac{4\, q_{pV}\, M}{\pi d \eta R T} \tag{1.29}$$

where q_{pV} is the pV throughput (see Section 2.2).

If values of Re are inserted into this expression then the criteria for laminar flow can be stated in terms of q_{pV} and d. For example, flow will be laminar when Re < 2300, *i.e.* when:

$$\left(\frac{q_{pV}}{d}\right) < 1.8 \times 10^{3}\, \frac{\eta R T}{M}$$

Note that it is essential to use units consistently. For η in Pa s, R in Pa m^3 kmol^{-1} K^{-1} and M in kg kmol^{-1}, q_{pV} must be in Pa m^3 s^{-1} and d in m.

Example 1.20

What values would $\left(\frac{q_{pV}}{d}\right)$ have for the laminar flow of H_2 in a tube at 20 °C?

(η for H_2 at 20 °C is 0.88×10^{-5} Pa s)

$$Re = \frac{4}{\pi}\left(\frac{q_{pV}}{d}\right)\frac{M}{\eta R T}$$

For laminar flow, $Re < 2300$.

$$\therefore \left(\frac{q_{pV}}{d}\right)_{H_2, 20\,^\circ C} < \frac{1.8 \times 10^{3} \times \eta \times RT}{M}$$

$$< \frac{1.8 \times 10^{3} \times 0.88 \times 10^{-5}\ \text{Pa s} \times 8314\ \text{Pa m}^3\text{kmol}^{-1}\ \text{K}^{-1} \times 293\ \text{K}}{2\ \text{kg kmol}^{-1}}$$

$$< 19\,300\ \text{Pa m}^2\ \text{s}^{-1}$$

Example 1.21

Air at 25 °C (q_{pV} = 1870 mbar L s^{-1}) is being pumped through a DN 40 KF* pipe. Calculate Re if the dynamic viscosity for air is 1.87×10^{-5} Pa s.

$$Re = \frac{4 \times q_{pV}\, M}{\pi d \eta R T}$$

$$= \frac{4 \times 187\ \text{Pa m}^3\ \text{s}^{-1} \times 29\ \text{kg kmol}^{-1}}{\pi \times 4.1 \times 10^{-2}\ \text{m} \times 1.87 \times 10^{-5}\ \text{Pa s} \times 8314\ \text{Pa m}^3\ \text{kmol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}$$

$$= 3634 \text{ (flow is turbulent)}$$

---

* A comparison of nominal widths (DN) with internal diameters for standard fittings used in vacuum technology is given in the Appendix.

Example 1.22

The transition from viscous, laminar to turbulent flow starts at about $Re = 2300$ (no sharp boundary). Calculate the throughput at 25 °C for He ($\eta = 1.98 \times 10^{-5}$ Pa s, see Example 1.18) for a tube with $d = 50$ mm.

$$\begin{aligned} q_{pV} &= \frac{\mathrm{Re}\,\pi d \eta RT}{4M} \\ &= \frac{2100 \times \pi \times 0.05\,\mathrm{m} \times 1.98 \times 10^{-5}\,\mathrm{Pa\,s} \times 8314\,\mathrm{Pa\,m^3\,kmol^{-1}\,K^{-1}} \times 298\,\mathrm{K}}{4 \times 4\,\mathrm{kg\,kmol^{-1}}} \\ &= 1011\,\mathrm{Pa\,m^3\,s^{-1}} \\ &= \underline{1.01 \times 10^4\,\mathrm{mbar\,L\,s^{-1}}} \end{aligned}$$

1.8 GAS DYNAMICS

In vacuum technology, some calculations involve the steady flow of fluid through duct of changing circular cross-section (diffusers, jets, nozzles, *etc.*) and the methods of gas dynamics can be applied to calculate pressures, velocities and temperatures. (A criterion for the applicability of gas dynamics is that $Kn < 0.01$ although, according to ref. (d), the methods can be applied even at Kn values up to 0.3.)

A very useful equation to deal with phenomena associated with the flow of fluids is the Bernoulli equation. It can be used to analyse fluid flow along a streamline from a point 1 to a point 2 assuming that the flow is steady, the process is adiabatic and that frictional forces between the fluid and the tube are negligible. Various forms of the equation appear in textbooks on fluid mechanics and physics. A statement in differential form can be obtained:

$$-\int_1^2 \frac{\mathrm{d}p}{\rho} = \tfrac{1}{2}(v_2^2 - v_1^2) \tag{1.30}$$

where p, ρ and v are pressure, density and velocity, respectively, and the subscripts 1 and 2 refer to the initial and final states of the system, respectively. If the relationship between p and ρ is known, the integral can be evaluated and v_2 can be obtained from v_1. In an open system, if a mass (m) of working substance with volume V_1 and pressure p_1 enters the system and expands to $V_2 > V_1$ ($p_2 < p_1$), leaving with pressure p_2 and volume V_2 then

$$(h_1 - h_2) = \tfrac{1}{2}(v_2^2 - v_1^2) \tag{1.31}$$

where h_1 and h_2 are the initial and final specific enthalpies respectively.

For adiabatic changes in the state of an ideal gas, the following relationships exist:

$$\left(\frac{p_2}{p_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma} = \left(\frac{T_2}{T_1}\right)^{\gamma/\gamma-1} = \left(\frac{\rho_2}{\rho_1}\right)^{\gamma} \tag{1.32}$$

where $\gamma = c_p/c_v$ (the ratio of the specific heat capacities at constant pressure and volume).

From the equalities given in (1.32), it can be shown that:

$$\left(\frac{p_2}{p_1}\right) = \left(\frac{\rho_2}{\rho_1}\right)^{\gamma} \tag{1.33}$$

and

$$\frac{1}{\rho_2} = \frac{1}{\rho_1}\left(\frac{p_1}{p_2}\right)^{1/\gamma} \tag{1.34}$$

Further, the equation of state for an ideal gas can be rearranged to yield:

$$\frac{p}{\rho} = \frac{RT}{M}$$

Values of γ for a range of gases are given in Table 1.5.

Table 1.5 *General† and specific* values of γ for various gases*

Gas	$\gamma^{\dagger}$	γ^{*}
Monatomic	1.66	1.67 (Ar)
(*e.g.* He, Ar)		1.66 (He)
Diatomic	1.4	1.41 (H_2)
(*e.g.* N_2, O_2)		1.404 (N_2)
		1.401 (O_2)
Triatomic	1.3	1.28 (N_2O)
(*e.g.* CO_2, N_2O)		
Polyatomic	1.1	—

† Based on $\gamma = (f + 2)/f$ where f = number of degrees of freedom (f = 3 for monatomic gases).
* See ref. (h).

It can be shown that if a stagnant fluid ($v_1 = 0$, $T = T_1$) is expanded through a jet, from p_1 to p_2, the flow velocity in the streamline is given by:

$$v = \left(\frac{2\gamma}{\gamma - 1} \cdot \frac{RT_1}{M}\left[1 - \left(\frac{p_2}{p_1}\right)\right]^{(\gamma-1)/\gamma}\right)^{1/2} \tag{1.35}$$

indicating that v depends on T_1 and the expansion ratio (p_2/p_1).

The mass flux density (j_m) in the streamline can be obtained from the expression [arrived at in the derivation of Equation (1.30)]:

$$-\frac{\mathrm{d}p}{\mathrm{d}v^2} = \rho v \tag{1.36}$$

Differentiation of Equation (1.35) with respect to v gives:

$$j_m = \rho v = -\frac{\mathrm{d}p}{\mathrm{d}v} = p_1\left(\frac{2\gamma}{\gamma - 1}\cdot\frac{M}{RT_1}\left[\left(\frac{p_2}{p_1}\right)^{2/\gamma} - \left(\frac{p_2}{p_1}\right)^{(1+\gamma)/\gamma}\right]\right)^{½} \tag{1.37}$$

A critical condition can be defined where v has achieved the local velocity of sound ($Ma = 1$, where Ma is the Mach number = flow velocity/velocity of sound). At $Ma = 1$, the quantities j_m, ρ and v have reached critical values, indicated by *,

and
$$j_m^* = \rho^* v^* = -\frac{\mathrm{d}p}{\mathrm{d}v} = p_1\left(\frac{2}{\gamma + 1}\right)^{1/\gamma-1}\left(\frac{2\gamma}{\gamma + 1}\cdot\frac{M}{RT_1}\right)^{½} \tag{1.38}$$

Further useful expressions that can be derived are:

$$\frac{p^*}{p_1} = \left(\frac{2}{\gamma + 1}\right)^{\gamma/\gamma-1} \tag{1.39}$$

$$\frac{T^*}{T_1} = \frac{2}{\gamma + 1} \tag{1.40}$$

$$v^* = \left(\frac{RT_1}{M}\cdot\frac{2\gamma}{\gamma + 1}\right)^{½} \tag{1.41}$$

If a nozzle is considered in which stationary flow is established [where the properties of the gas (temperature, density, flow velocity) do not vary significantly over several mean free paths], the continuity equation (the throughput is the same through all sections) can be written:

$$Aj_m = A\rho v = q_m = \text{const} \tag{1.42}$$

where A is the cross-sectional area and a function of distance along the line of flow. j_m, ρ and v are also functions of distance. If, at a particular point in the nozzle (at cross-section A^*), v^* is reached and $Ma = 1$, then:

$$A\rho v = A^* \rho^* v^* \tag{1.43}$$

From equation (1.38), the mass throughout can be obtained:

$$q_m = A_{\min} p_1 \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\gamma-1}} \left(\frac{2\gamma}{\gamma+1}\cdot\frac{M}{RT_1}\right)^{1/2} \tag{1.44}$$

The equivalent expression for pV-throughput is:

$$q_{pV} = A_{\min} p_1 \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\gamma-1}} \left(\frac{2\gamma}{\gamma+1}\cdot\frac{RT_1}{M}\right)^{1/2} \tag{1.45}$$

For air at 293 K ($R = 83.14$ mbar L mol^{-1} K^{-1}):

$$q^*_{pV} = 20\, A_{\min}\, p_1$$

where q_{pV} has units of mbar L s^{-1} if p_1 is in mbar and $A_{\min}$ in cm^2.

Example 1.23

A helium compressor takes in He at a pressure of 15 bar, and a temperature of 20 °C and delivers it at a rate of 2.4 kg h^{-1} at a pressure of 22 bar. The inlet velocity is negligible. The helium in the delivery pipe (i.d. = 13 mm) is at 120 °C. Calculate the heat transfer between the compressor and its surroundings when the power input to the compressor is 1.8 kW. Given $C_{p,\mathrm{He}} = 5.23$ kJ kg^{-1} K^{-1} and that He behaves ideally.

This can be solved using the steady-flow energy equation:

$$(h_2 - h_1) + \frac{1}{2}(v_2^2 - v_1^2) + g(z_2 - z_1) = q + w \tag{1.46}$$

where h_2, h_1 are the specific enthalpies of the gas in state 2 and state 1, v_2 and v_1 are the velocities of the gas in states 2 and 1, g is 9.8ms^{-2}, z_2 and z_1 are the heights of the outlet and inlet, respectively, w is work added to the gas/unit mass/unit time, q is heat added to the gas/unit mass/unit time.

Assume:

$$z_2 = z_1$$
$$\text{and } v_1 = 0$$

Values are required for v_2 and $(h_2 - h_1)$.
For v_2, volume swept out by He in 1 s

$$= A_{\text{inlet}}\,(\mathrm{m}^2) \times v_2\,(\mathrm{m\ s}^{-1})$$
$$= (1.33 \times 10^{-4}) v_2\ \mathrm{m}^3\,\mathrm{s}^{-1}$$

$$= \dot{m}\,(\mathrm{kg\,s^{-1}}) \times V_{\mathrm{He}}\,(\mathrm{m^3\,kg^{-1}})$$

$$\dot{m} = 2.4\,\mathrm{kg\,h^{-1}} = 6.67 \times 10^{-4}\,\mathrm{kg\,s^{-1}}$$

Specific volume for He is calculated from:

$$pV_{\mathrm{He}} = RT \text{ per kmol He}$$

$$\therefore \quad V_{\mathrm{He}} = \frac{8314\,\mathrm{Pa\,m^3\,kmol^{-1}\,K^{-1}} \times 393\,\mathrm{K}}{4\,\mathrm{kg\,kmol^{-1}} \times 22 \times 101325\,\mathrm{Pa}}$$
$$= 0.37\,\mathrm{m^3\,kg^{-1}}$$

So volume flow rate $= 6.67 \times 10^{-4} \times 0.37\,\mathrm{m^3\,s^{-1}}$

$$\text{and} \quad v_2 = \frac{6.67 \times 10^{-4} \times 0.37\,\mathrm{m^3\,kg^{-1}}}{1.33 \times 10^{-4}\,\mathrm{m^2}} = 1.9\,\mathrm{m\,s^{-1}}$$

Term $\frac{1}{2}v_2^2$ will be negligible compared to enthalpy change

$$\therefore \quad \dot{m}(h_2 - h_1) = \dot{Q} + \dot{W}$$

$$\therefore \quad \dot{m}\,c_p(T_2 - T_1) = \dot{Q} + 1800\,\mathrm{W}$$

$$\therefore \quad 2.4\,\mathrm{kg\,h^{-1}} \times 5230\,\mathrm{J\,kg^{-1}\,K^{-1}} \times 100\,\mathrm{K} = \dot{Q} + 1800\,\mathrm{W}$$
$$348.6\,\mathrm{W} = \dot{Q} + 1800\,\mathrm{W}$$
$$\therefore \dot{Q} = \underline{-1.45\,\mathrm{kW}}$$

The significance of the above can be illustrated if we consider an orifice through which gas can expand into a vacuum chamber. If the inlet pressure (p_0) is fixed but the chamber pressure can be varied then, on gradual reduction of the pressure in the chamber, the mass flow through the nozzle increases. When the chamber pressure is p^*, the mass flow reaches its maximum value (q_m^*). Subsequent pressure reduction would not affect q_m^*. This is known as choked- or blocked flow.

Example 1.24

A vacuum chamber is vented using argon at 20 °C and standard atmospheric pressure. It flows into the chamber *via* a nozzle of 2 mm diameter. Calculate (i) the critical pressure (ii) the critical velocity (v^*) and (iii) the mass flux of the gas.

(i) From Equation (1.39):

$$\frac{p^*}{p_1} = \left(\frac{2}{\gamma + 1}\right)^{\gamma/(\gamma-1)}$$

where $p_1 = 1013\,\text{mbar}$ and $\gamma = 1.66$ (Table 1.5)

$$\therefore \quad \text{p}^* = \left(\frac{2}{2.66}\right)^{1.66/0.66}$$

$$= 0.488$$

$$\therefore \quad p^* = 0.488 \times 1013\,\text{mbar}$$
$$\underline{= 494.5\,\text{mbar}}$$

(ii) From Equation (1.41):

$$v^* = \left(\frac{RT_1}{M} \cdot \frac{2\gamma}{\gamma + 1}\right)^{1/2}$$

$$= \left(\frac{8314\,\text{Pa m}^3\,\text{kmol}^{-1}\,\text{K}^{-1} \times 293\,\text{K} \times 3.32}{40\,\text{kg kmol}^{-1} \times 2.66}\right)^{1/2}$$

$$\underline{= 275.7\,\text{m s}^{-1}}$$

(iii) $$q_\text{m} = A_\text{min} p_1 \left(\frac{2}{\gamma + 1}\right)^{1/(\gamma-1)} \left(\frac{2\gamma}{\gamma + 1} \cdot \frac{M}{RT_1}\right)^{1/2}$$

$$A_\text{min} = 3.14 \times 10^{-6}\ \text{m}^2$$

$$\therefore \quad q_\text{m} = (3.14 \times 10^{-6})\text{m}^2 \times 101\,325\,\text{Pa} \times \left(\frac{2}{2.66}\right)^{1/0.66} \sqrt{\frac{3.32}{2.66} \cdot \frac{1}{60900\,\text{m}^2\,\text{s}^{-2}}}$$

$$= 9.34 \times 10^{-4}\,\text{kg s}^{-1}$$
$$\underline{= 0.93\,\text{g s}^{-1}}$$

Example 1.25

Air at 20 °C and 1 standard atmosphere pressure is required to expand through a valve at a rate of $18.7\,\text{g s}^{-1}$ into a large chamber at 10 mbar. Assuming the inlet velocity is negligible, calculate the diameter of the orifice of the valve.

From the previous example, the critical pressure for air at 1013 mbar is 535 mbar. This means that flow through the valve is choked until the chamber pressure increases to 535 mbar.

Under choked conditions, the maximum flux of gas through the valve is q_m^*:

$$q_\text{m}^* = A \cdot j_\text{m}^*$$

$$q_\text{m}^* = A_\text{valve}\, p_0 \left(\frac{2}{\gamma + 1}\right)^{1/(\gamma-1)} \left(\frac{2\gamma}{\gamma + 1} \cdot \frac{M}{RT_0}\right)^{\frac{1}{2}}$$

So $A_{\text{valve}} = 0.0187\,\text{kg s}^{-1}/(101\,325\,\text{Pa} \times 0.63 \times (3.73 \times 10^{-3})(\text{ms}^{-1})$

This gives: $A_{\text{valve}} = 7.86 \times 10^{-5}\,\text{m}^2$

hence $\underline{d_{\text{orifice}} = 10\,\text{mm}}$

A useful result that can be obtained from the choked and non-choked throughput equations is the time to vent a vacuum chamber to atmospheric pressure through an orifice or a short duct:

$$t_{\text{vent}} = \frac{V}{C_{\text{ap}}}\sqrt{\frac{\gamma + 1}{\pi\gamma}} \tag{1.47}$$

where t_{vent} is the venting time (s), V is the volume (L) and C_{ap} is the molecular flow conductance of an aperture ($\bar{c}/4$) which for air at 20 °C = 11.6 $\text{L s}^{-1}\,\text{cm}^{-2}$ (ref. R.G. Livesey, p. 81 in ref. (f)). This assumes an isothermal process. In fact, with rapid venting, the resulting chamber temperature often exceeds that of the initial temperature of the venting gas being introduced.

CHAPTER 2

Gas Flow

2.1 INTRODUCTION

Chapter 2 begins by defining essential terms in vacuum technology – gas flow rate, pumping speed, conductance, *etc.* It also emphasises a basic assumption for calculation – that continuity is established in a system (what enters must eventually leave). Simple equations are stated and their use demonstrated.

In Chapter 1, the types of gas flow that could be established in vacuum systems were defined. This chapter deals with the quantification of viscous and molecular flow for simple, model systems (pipelines of constant, circular cross-section, orifices and apertures, *etc.*). These are nevertheless useful, and worked examples are presented to encourage users to quantify existing or proposed systems and to provide reassurance that calculations are not only relatively straightforward but very useful indeed.

Flow in the range between viscous and molecular types (sometimes termed Knudsen flow) is also mentioned but quantified only for tubes. It is, however, an additional check for vacuum technologists who tend only to look at the limiting cases to obtain upper and lower values for parameters.

2.2 DEFINITIONS

Gas flow rate (gas flux) is expressed in various ways in vacuum technology. The symbols q and Q are commonly used and Table 2.1 contains four definitions.

The useful quantity, pV-throughput (q_{pV}), must be associated with a specified temperature if the true gas flow rate is to be defined.

Pumping speed (typical units $\mathrm{L\,s^{-1}}$; $\mathrm{m^3\,h^{-1}}$) generally refers to the volume rate of flow of gas entering the vacuum pump. Manufacturers state the pumping speed of a pump at the inlet of the pump (S_0, in this

Table 2.1 *Expressions for gas flow rate*

Quantity	*Equation*		*Typical units*[a]
Mass flow rate	$q_m = \frac{\Delta m}{\Delta t}$	(2.1)	$\mathrm{kg\,s^{-1}}$
pV flow rate (pV-throughput)	$q_{pV} = p\dot{V}$; $= p\frac{\Delta V}{\Delta t}$	(2.2)	$\mathrm{mbar\,L\,s^{-1}}$, $\mathrm{Pa\,m^3\,s^{-1}}$
Volume flow rate	$q_V = \dot{V}$ $= \frac{\Delta V}{\Delta t}$	(2.3)	$\mathrm{m^3\,h^{-1}}$, $\mathrm{L\,s^{-1}}$
Molar flow rate[b]	$q_n = \dot{n}$ $= \frac{\Delta n}{\Delta t}$	(2.4)	$\mathrm{mol\,s^{-1}}$

[a] Expressions such as L/s, $\frac{\mathrm{L}}{\mathrm{s}}$ and $\mathrm{L\,s^{-1}}$ are equivalent.

[b] n is defined in $pV = nRT$ where $n = \frac{m}{M}$.

book). As pipework, valves, *etc.* present a resistance to gas flow, the *effective* pumping speed (S_{eff}) represents the local volume rate of flow of gas. S_{eff} is always smaller than S_0.

The relationship between S_0 and S_{eff} is given by:

$$\frac{1}{S_{\text{eff}}} = \frac{1}{S_0} + \frac{1}{C_{\text{tot}}} \tag{2.5}$$

where C_{tot} refers to the total conductance of all the pipework, valves, filters *etc.* between the system and the pump(s). (The inverse of flow resistance is the conductance.)

The *conductance* of a component (by analogy with Ohm's law) is given by

$$C = \frac{q_{pV}}{\text{pressure difference across the component}} \tag{2.6}$$

The units of conductance depend on the units used to express throughput.

For pV-throughput, C is expressed in $\mathrm{L\,s^{-1}}$ or $\mathrm{m^3\,h^{-1}}$.

In Figure 2.1, a chamber of volume V at a uniform pressure p is connected to a pump *via* a tube of conductance C. (The numerical value of C depends on the type of flow in the system.) The pressure is maintained against a gas flow $q_{pV,\text{in}}$ entering the system. $q_{pV,\text{in}}$ may arise in

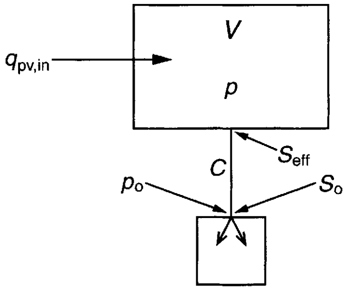


Figure 2.1 *Schematic diagram of a basic vacuum system*
Note: The symbols used in this book are generally according to ISO3753:1977 (BS 5543:1978): see the Appendix on p. 225.

various ways. It may be due to leakage, added process gas, outgassing from the system and any added substrates or permeation through the seals, or any combination of these.

In vacuum technology, it is usual to assume that there is continuity throughout the system and the throughput is the same in all sections.

From a steady-state flux balance of the flow entering the system and the flow into the pump, S_{eff} can be defined as:

$$S_{\mathrm{eff}} = \frac{q_{pV,\mathrm{in}}}{p} \tag{2.7}$$

and

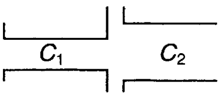
$$q_{pV,\mathrm{pump}} = p \times S_{\mathrm{eff}} \tag{2.7a}$$

To obtain an effective pumping speed of 90% or more of S_0, rearrangement of the relationship between S_{eff}, S_0 and C_{tot} yields:

$$\frac{S_{\mathrm{eff}}}{S_0} = \frac{1}{\left(1 + \frac{S_0}{C_{\mathrm{tot}}}\right)} \tag{2.8}$$

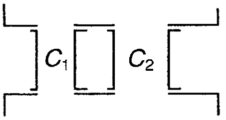
and shows that C_{tot} has be to larger than S_0 by a factor of 10.

The contribution to C_{tot} of the conductances of the individual components depends on whether they are connected in series or in parallel. For series connection:



$$\frac{1}{C_{\text{tot}}} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \ldots \tag{2.9}$$

For parallel connection:



$$C_{\text{tot}} = C_1 + C_2 + C_3 + \ldots \tag{2.10}$$

Formulae exist to allow conductances to be calculated for simple shapes, *e.g.* straight tubes of circular cross-section. For complex items, *e.g.* baffles, or for a series of components, it may be better to calculate the conductance from the pressure difference established across the conductance under conditions of steady gas throughput. Manufacturers often state values for the conductance of valves, baffles, *etc.* in their literature. These values refer to the conductance under conditions of molecular flow (p-independent) for N_2.

Example 2.1

A vessel at 20 °C is connected to a vacuum pump (S_0 for air = 25 m^3/h) via a DN25 tube. The length of the tube is such that the pumping speed of the pump is reduced by 20%.

(a) If the pressure in the vessel is 2 mbar, calculate the minimum conductance of the tube.
(b) What is the nature of gas flow in the tube under these conditions?

(a)

$$S_{\text{eff}} = S_0 - 20\% = 20\,\text{m}^3/\text{h}$$

$$\frac{1}{S_{\text{eff}}} = \frac{1}{S_0} + \frac{1}{C_{\text{tube}}}$$

$$\therefore \quad \underline{C_{\text{tube}} = 100\,\text{m}^3/\text{h}\ (= 28\,\text{L s}^{-1})}$$

(b) Gas flow is defined by $Kn = \bar{l}/d$ (see Table 1.4, page 22).
To find $\bar{l}$, $\bar{p}$ (the mean pressure) in the tube must be found.
From Equation (2.6):

$$q_{pV,\text{tube}} = C_{tube}(\Delta p)_{\text{tube}}$$

$$\begin{aligned} q_{pV,\text{tube}} &= p_{\text{in}}\, S_{\text{eff}} \text{ (continuity equation)} \\ &= 2\,\text{mbar} \times 20\,\text{m}^3/\text{h} \end{aligned}$$

$$= 11\ \text{mbar L s}^{-1}$$

$$(\Delta p)_{\text{tube}} = 11\ \text{mbar L s}^{-1} / 28\ \text{L/s}$$
$$= 0.4\ \text{mbar}$$

If $P_{\text{in}} = 2\ \text{mbar}$

$P_{\text{out}} = 1.6\ \text{mbar}$

and $\bar{p} = 1.8\ \text{mbar}$

For air at 20 °C, $\bar{l}p \sim 6.5 \times 10^{-5}$ m.mbar. (see Table 1.2, page 15)
At 1.8 mbar:

$$\bar{l} = 6.5 \times 10^{-3}\ \text{cm mbar}/1.8\ \text{mbar}$$
$$= 3.6 \times 10^{-3}\ \text{cm}$$

$$\therefore\ Kn = 3.6 \times 10^{-3}\ \text{cm}/2.4\ \text{cm}$$
$$\underline{= 1.5 \times 10^{-3}}$$

Flow is, therefore, continuum (viscous) flow.
From Equation (1.29):

$$Re = \frac{4 q_{pV} M}{\pi d \eta RT}$$
$$= \frac{4 \times 1.1\ \text{Pa m}^3\text{s}^{-1} \times 29\ \text{kg kmol}^{-1}}{\pi \times 2.4 \times 10^{-2}\ \text{m} \times 1.87 \times 10^{-5}\ \text{Pa s} \times 8314\ \text{Pa m}^3\ \text{kmol}^{-1}\ \text{K}^{-1} \times 293\ \text{K}}$$
$$= 38$$

∴ Flow is viscous, laminar.
Another expression for *Re* is:

$$Re = (k)\frac{q(\text{mbar L/s})}{B\,\text{mm}}$$

where, for a tube of circular cross-section, $k = 261.5$ and $B = 2\pi d$ (perimeter of tube).
Using this gives:

$$\underline{Re = 37}$$

Example 2.2

A vacuum chamber is pumped by a turbomolecular pump ($S_{\text{eff}} = 250\ \text{L s}^{-1}$). Connected to the chamber *via* an aperture is a mass spectrometer for gas analysis. The MS is maintained at 2×10^{-5} mbar with a turbomolecular pump with an effective speed of 50 L s^{-1}. Ar is admitted to the main chamber to maintain the pressure at 5×10^{-3} mbar. Calculate the aperture conductance.

In the MS, $q_{pV} = p \times S_{\text{eff}} = 2 \times 10^{-5}\,\text{mbar} \times 50\,\text{L s}^{-1} = 10^{-3}\,\text{mbar L s}^{-1}$
From the conductance definition:

$$q_{\text{ap}} = C_{\text{ap}}\,(\Delta p)$$

$$\therefore \quad C_{\text{ap}} = \frac{q_{\text{ap}}}{\Delta p}$$

$$= \frac{10^{-3}\,\text{mbar L s}^{-1}}{(5 \times 10^{-3} - 2 \times 10^{-5})\,\text{mbar}}$$

$$= \frac{10^{-3}\,\text{mbar L s}^{-1}}{5 \times 10^{-3}\,\text{mbar}}$$

$$\underline{= 0.2\,\text{L s}^{-1}}$$

Example 2.3

In a vacuum chamber at 20 °C, the rate of water vapour desorption is $5 \times 10^{-2}\,\text{mbar L s}^{-1}$. The chamber has an overall leakage rate of $1 \times 10^{-2}\,\text{mbar L s}^{-1}$. An attached turbomolecular pump (TMP) has an effective, gas-independent speed of 1500 L s^{-1}.

(a) What pressure can be achieved?
(b) It is proposed to work at 1×10^{-6} mbar by fitting a liquid-nitrogen-cooled (LN_2-cooled) trap inside the chamber. If the gas loads remain the same, can this be achieved?

(a)

$$\begin{aligned} q_{pV,\text{tot}} &= q_{pV,\text{outgas}} + q_{pV,\text{leakage}} \\ &= 5 \times 10^{-2}\,\text{mbar L s}^{-1} + 1 \times 10^{-2}\,\text{mbar L s}^{-1} \\ &= 6 \times 10^{-2}\,\text{mbar L s}^{-1} \end{aligned}$$

∴ Achievable p_{tot}

$$= q_{pV,\text{tot}}/S_{\text{eff}}$$

$$\underline{p_{\text{tot}} \quad = 4 \times 10^{-5}\,\text{mbar}}$$

(b)

$$\begin{aligned} q_{pV,\text{tot}} &= q_{pV,\text{outgas}} + q_{pV,\text{leakage}} \\ &= 6 \times 10^{-2}\,\text{mbar L s}^{-1} \end{aligned}$$

The LN_2-cooled surface will only remove water vapour. The non-condensables will be pumped by the TMP.

$$p_{\text{tot}} = p_{\text{cond}} + p_{\text{non-cond}}$$

$$\therefore \quad p_{\text{tot}} = \frac{5 \times 10^{-2}\,\text{mbar L s}^{-1}}{S_{\text{eff,LN}_2}} + \frac{1 \times 10^{-2}\,\text{mbar L s}^{-1}}{1500\,\text{L s}^{-1}} = P_{\text{cond}} + 6.7 \times 10^{-6}\,\text{mbar}$$

The proposed pressure is exceeded by the contribution from the non-condensable gas load (6.7 × 10^{-6} mbar), *i.e.* the proposed pressure cannot be reached.

Example 2.4

In Example 2.3, the given leakage rate has been reduced to 1 × 10^{-3} mbar L s^{-1}. Can the original objective now be achieved and, if so, what should be the minimum surface area of the cold trap?

$$q_{pV,\text{tot}} = 5 \times 10^{-2}\,\text{mbar L s}^{-1} + 1 \times 10^{-3}\,\text{mbar L s}^{-1}$$

$$\therefore \quad p_{\text{tot}} = \frac{5 \times 10^{-2}\,\text{mbar L s}^{-1}}{S_{\text{eff,LN}_2}} + \frac{1 \times 10^{-3}\,\text{mbar L s}^{-1}}{1500\,\text{L s}^{-1}}$$

$$\therefore \quad 1 \times 10^{-6}\,\text{mbar} = \frac{5 \times 10^{-2}\,\text{mbar L s}^{-1}}{S_{\text{eff,LN}_2}} + 7 \times 10^{-7}\,\text{mbar}$$

$$\therefore \quad S_{\text{eff,LN}_2} = \frac{5 \times 10^{-2}\,\text{mbar L s}^{-1}}{3 \times 10^{-7}\,\text{mbar}}$$

$$= 1.7 \times 10^{5}\,\text{L s}^{-1}$$

The LN_2-cooled trap will only condense water vapour. The area-related pumping speed of the trap for water is (from Equation (1.13)):

$$S_{\text{LN}_2} = \frac{A\bar{c}}{4}$$

$$\bar{c}_{\text{H}_2\text{O}} = 145.5\sqrt{\frac{293}{18}}\,\text{m s}^{-1}$$

$$\frac{\bar{c}_{\text{H}_2\text{O}}}{4} = 146.8\,\text{m s}^{-1}$$

$$\therefore \quad A_{\text{LN}_2} = \frac{1.7 \times 10^{5}\,\text{L s}^{-1}}{146.8\,\text{m s}^{-1}}$$

$$= \frac{1.7 \times 10^{5}\,\text{L s}^{-1}}{14.7\,\text{L s}^{-1}\,\text{cm}^{-2}}$$

$$= \underline{11\,565\,\text{cm}^{2}}$$

Example 2.5

In a drying process, an air + water vapour mixture at 65 °C is produced with a total pressure of 80 mbar. If the mass flows of the vapour and air are 2.5 kg h^{-1} and 0.15 kg h^{-1}, respectively, what are the partial pressures of air and water vapour in the mixture?

$$\begin{aligned} q_{pV,\mathrm{tot}} &= q_{pV,\mathrm{air}} + q_{pV,\mathrm{H_2O}} \\ q_{pV,\mathrm{air}} &= p_{\mathrm{air}}\dot{V} = (\dot{m}_{\mathrm{air}}/M_{\mathrm{air}}) \times RT \\ q_{pV,\mathrm{H_2O}} &= p_{\mathrm{H_2O}}\dot{V} = (\dot{m}_{\mathrm{H_2O}}/M_{\mathrm{H_2O}}) \times RT \end{aligned}$$

$$\therefore \quad \frac{p_{\mathrm{air}}}{p_{\mathrm{tot}}} = \frac{q_{pV,\mathrm{air}}}{q_{pV,\mathrm{air}} + q_{pV,\mathrm{H_2O}}} = \frac{\dot{m}_{\mathrm{air}}/M_{\mathrm{air}}}{\dot{m}_{\mathrm{air}}/M_{\mathrm{air}} + \dot{m}_{\mathrm{H_2O}}/M_{\mathrm{H_2O}}}$$

$$\text{and} \quad \frac{p_{\mathrm{H_2O}}}{p_{\mathrm{tot}}} = \frac{q_{pV,\mathrm{H_2O}}}{q_{pV,\mathrm{air}} + q_{pV,\mathrm{H_2O}}} = \frac{\dot{m}_{\mathrm{H_2O}}/M_{\mathrm{H_2O}}}{\dot{m}_{\mathrm{air}}/M_{\mathrm{air}} + \dot{m}_{\mathrm{H_2O}}/M_{\mathrm{H_2O}}}$$

$$\frac{p_{\mathrm{air}}}{80\,\mathrm{mbar}} = \frac{150\,\mathrm{g\,h^{-1}}/29\,\mathrm{g\,gmol^{-1}}}{150\,\mathrm{g\,h^{-1}}/29\,\mathrm{g\,gmol^{-1}} + 2500\,\mathrm{g\,h^{-1}}/18\,\mathrm{g\,gmol^{-1}}}$$

$$\underline{\therefore \quad p_{\mathrm{air}} = 2.9\,\mathrm{mbar}}$$

$$p_{\mathrm{tot}} = p_{\mathrm{air}} + p_{\mathrm{H_2O}}$$

$$\text{So} \quad \underline{p_{\mathrm{H_2O}} = 77.1\,\mathrm{mbar}}$$

2.3 VISCOUS (CONTINUUM) FLOW

2.3.1 Viscous Flow in Tubes and Ducts

Relatively straightforward solutions can be obtained for the viscous flow of incompressible fluids in ducts of constant cross-section flowing at relatively low velocities.

Compressibility in gases can be ignored if $(Ma)^2 << 1$ where:

$$Ma = \frac{\text{gas flow velocity}}{\text{local velocity of sound}} \tag{2.11}$$

For example, Ma <0.3 meets the above criterion for incompressibility.

2.3.1.1 Circular Cross-section Pipes. In contrast to nozzles and apertures, the calculation of gas flow through tubes ($l >> d$) has to take the effects of gas viscosity into account. For smooth-walled tubes, gas fluxes less than $q^*/3$ and laminar flow conditions, the well-known expression for pV-throughput, can be obtained:

$$q_{pV} = \frac{\pi}{128\eta}\frac{d^4}{l}\left(\frac{p_0^2 - p_2^2}{2}\right) \tag{2.12}$$

where p_0 = upstream (higher) pressure, p_2 = downstream (lower) pressure and η = dynamic viscosity.

Note: a tube is regarded as smooth if the surface features on the wall do not exceed 1%d and Re is less than 10^5.

The term $\frac{(p_0^2 - p_2^2)}{2}$ in Equation (2.12) can be expressed as:

$$(p_0 - p_2) \times \frac{(p_0 + p_2)}{2} = \Delta p \times \bar{p}$$

where Δp = pressure difference and $\bar{p}$ = mean pressure. So (from Equation (2.6)):

$$C_{\text{tube}} = \frac{\pi}{128\eta}\frac{d^4}{l}\bar{p} \tag{2.13}$$

For air at 20 °C, $\eta = 18.2 \times 10^{-8}$ mbar s (1.82×10^{-5} Pa s), the equation for q_{pV} becomes:

$$q_{pV} = 135\frac{d^4}{l}\frac{(p_0^2 - p_2^2)}{2}\ \text{mbar L s}^{-1} \tag{2.14}$$

For Equations (2.14)–(2.18), l and d are in cm and p in mbar.

For other gases at other temperatures:

$$C_{\text{gas}} = C_{\text{air,20}\,°\text{C}} \times \frac{\eta_{\text{air,20}\,°\text{C}}}{\eta_{\text{gas},T}} \tag{2.15}$$

where

$$C_{\text{air,20}\,°\text{C}} = 135\,\frac{d^4}{l}\cdot\bar{p}\ \text{L s}^{-1} \tag{2.16}$$

Under some circumstances, choked flow can occur in a tube under viscous flow conditions. For laminar choked flow of air at 20 °C, the critical pressure p_2^* is given by:

$$p_2^* = 2.3\,\frac{d^2}{l}\,p_0^2 \tag{2.17}$$

The pV-throughput under choked flow conditions, is given by:

$$q_{pV} = 135\frac{d^4}{l}\frac{(p_0^2 - p_2^{*2})}{2}\ \text{mbar L s}^{-1} \tag{2.18}$$

if d and l are in cm and p is in mbar.

Example 2.6

Air is removed from a chamber at 5.1 mbar using a pump with an inlet speed of 100 m^3 h^{-1}. If the pipework is 10 m × DN63, confirm that the flow is viscous, laminar and calculate the effective speed of the pump at the chamber.

p at the pump inlet (p_{pump}) will always be lower than the pressure in the chamber (p_{ch}).
Calculate Kn using $\bar{l}\,p = 6.5 \times 10^{-3}$ cm mbar; it will be confirmed that the flow is viscous.
An evaluation of q_{pV}/d for air 20 °C assuming $q_{pV} \sim 5 \times 27.77$ mbar L s^{-1} gives a value of 20, well below the value where turbulence starts. The flow in the tube is, therefore, viscous, laminar.

Choking will not occur since, from Equation (2.17):

$$
\begin{aligned}
p^* &= \frac{2.3 \times 7^2 \times 5.1^2}{1000}\,\text{mbar} \\
&= \underline{2.9\,\text{mbar}}
\end{aligned}
$$

$$i.e.\quad p^* < p_{\text{ch}}$$

From Equation (2.16):

$$
\begin{aligned}
C_{\text{tube}} &= 135\frac{d^4}{l}\left(\frac{p_{\text{ch}} + p_{\text{pump}}}{2}\right) \\
&= 324\left(\frac{p_{\text{ch}} + p_{\text{pump}}}{2}\right)
\end{aligned}
$$

With a relatively high chamber pressure and a tube of large diameter, it can be assumed that:

$$p_{\text{ch}} \approx p_{\text{pump}} \text{ and } \bar{p} = 5\,\text{mbar}$$

$$
\begin{aligned}
C_{\text{tube}} &= 324 \times 5\,\text{L s}^{-1} \\
&= 1620\,\text{L s}^{-1}
\end{aligned}
$$

$$\therefore\quad \frac{1}{S_{\text{eff}}} = \frac{1}{S_0} + \frac{1}{1620} = \frac{1}{27.77} + \frac{1}{1620}\,\text{L s}^{-1}$$

$$\therefore\quad \underline{S_{\text{eff}} = 27.3\,\text{L s}^{-1}\ (98.3\,\text{m}^3\,\text{h}^{-1})}$$

Example 2.7

Air at 20 °C is evacuated from a chamber using a rotary vane pump (S_0 = 240 m^3 h^{-1}) *via* a 10 m × DN63 tube. If the pressure at the pump inlet is 6 mbar, calculate p_{ch} (pressure in the chamber) and S_{eff}.

Re can be calculated from Equation (1.29). Using the above values, together with the value of η given in Example 1.21, a value of *Re* = 455 is obtained. Therefore, viscous, laminar flow is established in the pipework.

$$
\begin{aligned}
C_{\text{tube}} &= 135\frac{d^4}{l}(\bar{p}) \\
&= \frac{135\times 7^4}{10^3}\left(\frac{p_{\text{ch}}+p_{\text{pump}}}{2}\right)\,\text{L s}^{-1} \\
&= 324\left(\frac{p_{\text{ch}}+p_{\text{pump}}}{2}\right)\,\text{L s}^{-1} \\
S_0 &= 240\,\text{m}^3\,\text{h}^{-1} = 67.77\,\text{L s}^{-1}
\end{aligned}
$$

From Equation (2.7a):

$$
\begin{aligned}
q_{pV,\,\text{pump}} &= S_0\times p_{\text{pump}} = 67.77\,\text{L s}^{-1}\times 6\,\text{mbar} \\
&= 400\,\text{mbar L s}^{-1}
\end{aligned}
$$

From Equation (2.6):

$$q_{pV} = C_{\text{tube}}\times(p_{\text{ch}}-p_{\text{pump}}) = 400\,\text{mbar L s}^{-1}\ \text{(continuity equation)}$$

$$\therefore\quad C_{\text{tube}} = \frac{400\,\text{mbar L s}^{-1}}{(p_{\text{ch}}-p_{\text{pump}})} = 324\left(\frac{p_{\text{ch}}+p_{\text{pump}}}{2}\right)$$

$$
\begin{aligned}
\frac{800}{324} &= (p_{\text{ch}}^2 - p_{\text{pump}}^2) \\
2.5 &= (p_{\text{ch}}^2 - 36) \\
p_{\text{ch}} &= \underline{6.2\,\text{mbar}}
\end{aligned}
$$

Also

$$
\begin{aligned}
S_{\text{eff}}\times p_{\text{ch}} &= S_0\times p_{\text{pump}} \\
\therefore\quad S_{\text{eff}} &= \frac{400}{6.2}\,\text{L s}^{-1} \\
S_{\text{eff}} &= \underline{64.5\,\text{L s}^{-1}(232\,\text{m}^3\,\text{h}^{-1})}
\end{aligned}
$$

Example 2.8

A vessel containing air at 30 mbar and 20 °C is evacuated through a DN10 pipe of 1 m length using an $18\,\text{m}^3\,\text{h}^{-1}$ pump. What is the effective speed of the pump?

Flow through the pipe is under viscous, laminar conditions (see Example 2.6 for typical assessment). From Equation (2.17), the onset of choked flow would require a pressure:

$$
\begin{aligned}
p^* &= 2.3\frac{d^2}{l}\,p_{\mathrm{ch}}^2 \\
&= \frac{2.3 \times 1 \times 30^2}{100} \\
&\approx 21\,\mathrm{mbar}
\end{aligned}
$$

This value will not be needed in the present calculation since, with the pipe of the given dimensions, p_{pump} will be almost 30 mbar.
From Equation (2.16):

$$
\begin{aligned}
C_{tube} &= 135\frac{d^4}{l}\bar{p} \\
&= \frac{135 \times 1^4\,\mathrm{cm}^4 \times 30\,\mathrm{mbar}}{100\,\mathrm{cm}}\,\mathrm{L\,s^{-1}} \\
&= 40.5\,\mathrm{L\,s^{-1}}
\end{aligned}
$$

$$
\frac{1}{S_{\mathrm{eff}}} = \frac{1}{S_0} + \frac{1}{C_{\mathrm{tube}}}
$$

$$
\therefore \quad S_{\mathrm{eff}} \; \underline{= 4.5\,\mathrm{L\,s^{-1}}\;(16\,\mathrm{m^3\,h^{-1}})}
$$

For *turbulent viscous* flow in smooth tubes:

$$
q_{pV} = d\left[\frac{\pi^2 \times 20}{16 \times 3.2} \times \frac{d^3(p_0^2 - p_2^2)}{2l}\right]^{4/7} \times \left(\frac{RT}{M}\right)^{3/7} \times \left(\frac{4}{\pi\eta}\right)^{1/7}
$$

For air at 20 °C, this reduces to:

$$
q_{pV} = 134d\left(\frac{d^3}{l}\,\frac{(p_0^2 - p_2^2)}{2}\right)^{4/7}\ \mathrm{mbar\,L\,s^{-1}} \tag{2.19}
$$

when l and d are in cm and p is in mbar.

For *choked turbulent flow*:

$$
q_{pV}^* = 134d\left(\frac{d^3(p_0^2 - p_2^{*2})}{2l}\right)^{4/7} \tag{2.20}
$$

where

$$
p^* = \frac{4.51\left(\dfrac{d^3 p_0^2}{2l}\right)^{4/7}}{d} \tag{2.21}
$$

2.4 MOLECULAR FLOW

Molecular flow occurs under conditions where $Kn > 0.5$ – the mean free path of the particles exceeds the smallest dimension of the flow channel. Under such conditions, with thin-walled orifices, for example, gas particles will pass through almost without collision. With pipes and ducts, however, this is not the case. Particularly for low Kn values (1–10) of the particles that enter the duct, some may reach the exit whilst the remainder return to the entrance after a number of collisions with the duct walls. What is important about such collisions is that, on collision with a wall, the particles are regarded as being immobilised for a very short time before emerging in any direction with equal probability (according to the cosine law). This describes diffuse or random scattering where no particular direction is favoured. To describe this process, the concept of 'transmission probability' (Pr) was introduced by Clausing.

In the case of an orifice, $Pr = 1$. For other types of pipes and ducts $Pr < 1$. A significant part of assessing molecular flow in ducts involves the estimation of Pr. An initial assumption is that molecules arrive at the entrance plane of a duct with an isotropic velocity distribution. Conductance under molecular flow conditions is independent of the pressure but obviously the throughput is proportional to the Δp as stated by the definition of C (*e.g.* Equation (2.6)).

2.4.1 Conductance of an Aperture

If it is assumed that $Pr = 1$, the molecular flow conductance is directly proportional to the rate of impingement of particles on the aperture area (A)

$$C_{\mathrm{ap}} = \frac{\bar{c}}{4} A \tag{2.22}$$

For air at 20 °C, $\bar{c} = 462.5\ \mathrm{m\ s^{-1}}$ and $\bar{c}/4 = 115.6\ \mathrm{m\ s^{-1}}$.

The area-related conductance can be derived as $115.6\ \mathrm{m^3\ s^{-1}}$ per $\mathrm{m^2}$ or:

$$C_{\mathrm{ap,air,20\,^\circ C}} = 11.6\ \mathrm{L\ s^{-1}\ cm^{-2}} \tag{2.23}$$

2.4.2 Conductance of Ducts and Tubes

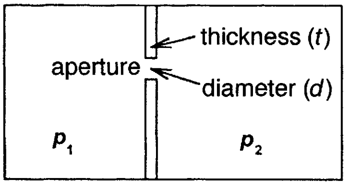
Generally, the conductance of a tube or a duct can be regarded as the conductance of the tube/orifice opening (C_{ap}) multiplied by a probability factor representing the proportion of particles leaving the exit of the conductance:

$$C_{\text{tube}} = C_{\text{ap}} \times Pr \qquad (2.24)$$

We shall consider two general cases.

2.4.2.1 Molecular Flow Conductance of an Orifice with Significant Wall Thickness (t).

$$C_{\text{ap}} = \frac{\bar{c}}{4} \mathrm{A}_{\text{ap}} \, Pr \qquad (2.25)$$



Let t be small compared to d. If $p_1 \gg p_2$ (in the appropriate pressure range) the particle flux through the aperture (area A) from p_1 to p_2 will be:

$$q_{N,\text{ap}} = \mathrm{n}_1 \frac{\bar{c}_1}{4} A_{\text{ap}} \qquad (2.26)$$

If, however, the same particles collide with the walls of the aperture, then the number of particles arriving at the wall will be:

$$q_{N,\text{wall}} = \frac{1}{2} \mathrm{n}_1 \frac{\bar{c}_1}{4} A_{\text{wall}}$$

since only half the space will contribute to particles interacting with the wall. Further, on desorption, there is an equal probability of returning to the entrance or leaving, so only half these particles may return to the entrance:

$$q_{N,\text{wall}} = \frac{1}{4} \mathrm{n}_1 \frac{\bar{c}_1}{4} A_{\text{wall}} \qquad (2.27)$$

The net particle flux through the orifice will be:

$$q_{N,\text{net}} = q_{N,\text{ap}} - q_{N,\text{wall}} \qquad (2.28)$$

$$= \frac{\mathrm{n}_1 \bar{c}_1}{4} A_{\text{ap}} - \frac{1}{4} \mathrm{n}_1 \frac{\bar{c}_1}{4} A_{\text{wall}} \qquad (2.29)$$

$$= \frac{\mathrm{n}_1 \bar{c}_1}{4} A_{\text{ap}} \left(1 - \frac{1}{4} \frac{A_{\text{wall}}}{A_{\text{ap}}}\right) \qquad (2.30)$$

Since $A_{\text{wall}} = \text{perimeter } (h) \times \text{wall thickness}$
$= h \times t$

$$q_{N,\text{net}} = \frac{\text{n}_1 \bar{c}}{4} A_{\text{ap}} \left(1 - \frac{1}{4}\frac{h\,t}{A_{\text{ap}}}\right)$$

$$= \frac{\text{n}_1\,\bar{c}}{4} A_{\text{ap}}\,Pr \tag{2.31}$$

where $Pr = \left(1 - \frac{1}{4}\frac{h\,t}{A_{\text{ap}}}\right)$

For a circular aperture, $A_{\text{wall}} = \pi dt$ and $A_{\text{ap}} = \pi r^2$, so

$$Pr = \left(1 - \frac{1}{4}\frac{2\pi r\,t}{\pi r^2}\right)$$

$$Pr = \left(1 - \frac{1}{2}\frac{\text{t}}{\text{r}}\right) \tag{2.32}$$

2.4.2.2 Molecular Flow through Tubes of Constant Cross-section. The conductance is determined by the rate at which particles enter the tube/duct and the probability that these molecules will be transmitted through the system.

According to Wutz *et al.* (ref. (d), p. 109) Pr is proportional to the ratio of a 'transmitting' area (A_{tr}), and an 'obstructing' area. The latter is proportional to the total surface area, *i.e.*:

$$Pr = \frac{A_{\text{tr}}}{A_{\text{tr}} + lh}$$

where h is the perimeter (circumference for a circular section tube) of the transmitting surface and l is length, giving $h \times l$ = total wall surface area.

$$\therefore \quad Pr = \left(1 + \frac{lh}{A_{\text{tr}}}\right)^{-1}$$

although further factors are introduced to take into account that A_{tr} is generally larger than the actual cross-section (A) and the obstructing area is smaller than the wall area ($h \times l$).

A formula which is widely used can be obtained from the above considerations:

$$C_{\text{tube/duct}} = C_{\text{ap}} \left(1 + \frac{3}{16}\frac{lh}{A}\right)^{-1} \tag{2.33}$$

For a tube of circular cross-section, this yields:

$$C_{\text{tube}} = C_{\text{ap}}\left(1 + \frac{3l}{8r}\right)^{-1} \tag{2.34}$$

Depending on the ratio (l/r), the above equation may require considerable correction (ref. (d)). A correction factor (ξ) is therefore introduced in the probability expression:

$$Pr = \left(1 + \frac{3}{8}\frac{l}{r}\right)^{-1} \xi^{-1} \tag{2.35}$$

which is given in Figure 2.2 as a function of (l/r).

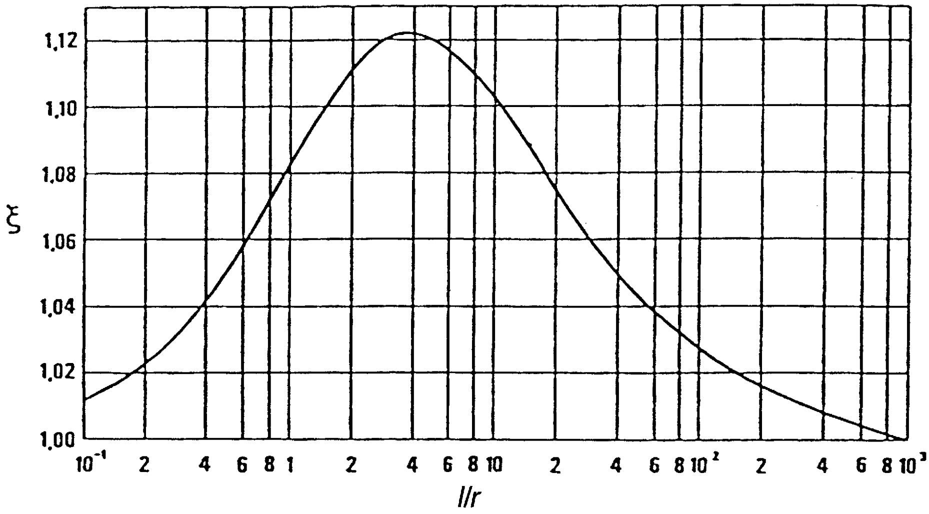


Figure 2.2 *Correction factor (ξ) for use with the expression for the conductance of a tube with circular cross-section*

(Reproduced from ref. (d), p. 109, with permission)

A shorter expression can be obtained for 'long' ($l \gg d$) tubes:

$$\begin{aligned} C_{\text{tube,long}} &= C_{\text{ap}}\left(1 + \frac{3}{4}\frac{l}{d}\right)^{-1} \\ &\cong \frac{\pi \bar{c}\, d^3}{12 l} \end{aligned} \tag{2.36}$$

For air at 20 °C, this further approximates to:

$$C_{\text{tube,long}} = 12.1 \frac{d^3}{l}\,\mathrm{L\,s^{-1}} \quad \text{when } d \text{ and } l \text{ are in cm.} \tag{2.37}$$

Example 2.9

A turbomolecular pump with a DN 63 ISO-K inlet has a pumping speed for N_2 of $115\,\mathrm{L\,s^{-1}}$. It is to be connected directly to a system used for obtaining outgassing data. For this application, the effective pumping speed of the pump is to be reduced to $50\,\mathrm{L\,s^{-1}}$ by inserting a plate with a circular aperture in the flange. Calculate the diameter of the aperture.

$$\frac{1}{S_{\mathrm{eff}}} = \frac{1}{S_0} + \frac{1}{C_{\mathrm{ap}}}$$

$$\therefore \quad \frac{1}{50} = \frac{1}{115} + \frac{1}{C_{\mathrm{ap}}}$$

$$\frac{1}{C_{\mathrm{ap}}} = \frac{1}{50} - \frac{1}{115}$$

$$C_{\mathrm{ap}} = 88.5\,\mathrm{L\,s^{-1}}$$

Also, from Equation 2.22, $C_{\mathrm{ap}} = \frac{\bar{c}}{4} A$.

From Example (1.9):

$$\bar{c}_{\mathrm{N_2,20\,^\circ C}} = 471\,\mathrm{m\,s^{-1}}$$

$$\therefore \quad C_{\mathrm{ap}} = 11.8\,\mathrm{L\,s^{-1}\,cm^{-2}} \times A\,\mathrm{cm^2}$$

$$A = 7.52\,\mathrm{cm^2}$$

$$\underline{d = 3.1\,\mathrm{cm}}$$

Example 2.10

A turbomolecular pump with an inlet speed $S_0 = 55\,\mathrm{L\,s^{-1}}$ (independent of gas type) is connected to a system by a 2m DN63 ISO-K pipe. Compare the values for C_{tube} obtained using Equations (2.35) and (2.37) and find the effective pumping speed (S_{eff}) in both cases.

From Equation (2.35):

$$C_{\mathrm{tube}} = C_{\mathrm{ap}} \times \frac{1}{\left(1 + \frac{3}{4}\frac{l}{d}\right)\xi}$$

where ξ is obtained from Figure 2.2.

Using Equation (2.23), *i.e.*:

$$C_{\mathrm{ap,air}} = 11.6\,\mathrm{L\,s^{-1}\,cm^{-2}}$$

so if $A_{\mathrm{ap}} = \pi d^2/4 = 38.5\,\mathrm{cm^2}$

then $\underline{C_{\mathrm{ap}} = 446\,\mathrm{L\,s^{-1}}}$

$$\therefore \quad C_{\text{tube}} = 446 \times \frac{1}{\left(1 + \frac{3}{4}\frac{200}{7}\right)\xi}$$

From Figure 2.2:

$$\frac{l}{r} = \frac{200}{3.5} \text{ and } \xi = 1.04$$

$$\therefore \quad C_{\text{tube}} = \underline{19.1\ \text{L s}^{-1}}$$

From Equation (2.37):

$$C_{\text{tube,long}} = \frac{12.1\text{d}^3}{l}\ \text{L s}^{-1} \text{ for air, where } l \text{ and } d \text{ are in cm.}$$

$$= \underline{20.8\ \text{L s}^{-1}}$$

$$S_{\text{eff,TMP}} = \frac{1}{\left(\frac{1}{S_0} + \frac{1}{C_{\text{tube}}}\right)}$$

$$= \underline{14.2\ \text{L s}^{-1} (26\%\ S_0)} \quad \text{using Equation (2.35)}$$

$$= \underline{15.1\ \text{L s}^{-1} (27\%)} \quad \text{using Equation (2.37)}$$

Conductance may be calculable for fairly simple geometries but with complex vacuum components such as baffles, filters, valves, *etc.*, it is not possible to calculate conductances analytically. Conductances of such objects are usually determined by measuring the pressure difference (Δp) across the object at a known throughput (q_{pV}):

$$q_{pV,T,\text{N}_2} = C_{\text{obj,N}_2}(\Delta p)$$

Manufacturers of vacuum components often state conductance values (for N_2 or air, under molecular flow conditions) for such products. If a conductance value, either calculated or measured, is known for gas A, its value for gas B (at the same temperature) is readily calculated. For example, under molecular flow conditions:

$$C_{\text{obj,A}} = C_{\text{ap,A}} Pr$$

where

$$C_{\text{ap,A}} = \frac{\bar{c}_{\text{A}} A}{4} \text{ and } \bar{c}_{\text{A}} = 145.5 \left(\frac{T}{M_{\text{A}}}\right)^{1/2}$$

Therefore, as:

$$C_{\mathrm{obj,B}} = C_{\mathrm{ap,B}} Pr$$

then

$$\frac{C_{\mathrm{obj,A}}}{C_{\mathrm{obj,B}}} = \sqrt{\frac{(M_{\mathrm{B}})}{(M_{\mathrm{A}})}}$$

or

$$C_{\mathrm{obj,B}} = C_{\mathrm{obj,A}} \left(\frac{M_{\mathrm{A}}}{M_{\mathrm{B}}}\right)^{½} \qquad (2.38)$$

Example 2.11

A DN40CF gate valve has a high vacuum conductance for N_2 of 220 L s^{-1}. What is the conductance for Ar?

$$\begin{aligned} C_{\mathrm{valve,Ar}} &= C_{\mathrm{valve,N_2}} \sqrt{\frac{28}{40}}\ \mathrm{L\ s^{-1}} \\ &= \underline{184\ \mathrm{L\ s^{-1}}} \end{aligned}$$

2.4.3 Molecular Flow through Components

In many applications, it is often necessary to attach pumps to systems *via* elbows or valves, or to shield devices to protect them from thermal radiation or X-rays. Some examples are given below.

2.4.3.1 Elbows, bent tubes. The use of right-angle bends in tubes of circular cross-section is widespread in vacuum technology. Calculations show that a tube of constant diameter with a right angle bend and sections l_1 and l_2 leading to and from the bend, will have a transmission probability equivalent to that of a straight tube of length $L = l_1 + l_2$ to within a few per cent.

In the case of curved tubes having a total length L, the transmission probability can be regarded as that of an equivalent straight tube of length L.

2.4.3.2 Baffles. The use of baffles (louvres/chevrons) is of significant practical interest. Baffles are used to reduce backstreaming with diffusion pumps and also to reduce thermal radiation in cryopump applications. They are also used to minimise the effects of X-radiation generated in, for example, electron beam welders.

In Figure 2.3, gas transmission probabilities (Pr) are shown for both chevron (a) and louvre (b) baffles.

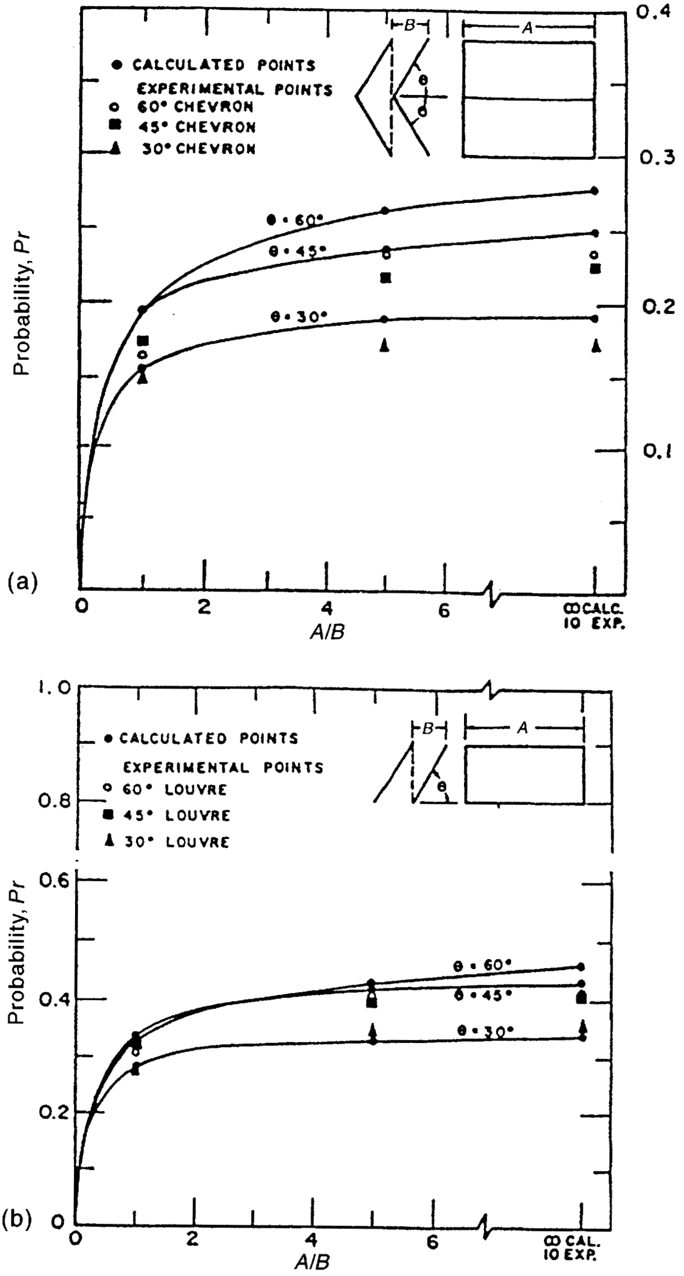


Figure 2.3 *Molecular gas transmission probabilities of baffles*
(Reproduced from Levenson, Milleron and Davies, *Vide* 1963, **103**, 42)

Example 2.12

A turbomolecular pump (S_0 = 200 L s^{-1} for N_2) is fitted to a mass spectrometer *via* 200 mm of pipe with a diameter of 102 mm (DN100). Calculate the pumping speed of the TMP at the mass spectrometer.

The conductance of such a pipe is given by:

$$C_{\text{tube}} = C_{\text{ap}} \times Pr$$

where *Pr* is given in equation (2.35).

An approximation can be obtained by assuming C_{ap} for the connecting tube can be calculated from Equation (2.23):

$$C_{\text{ap,air,20\,°C}} = 11.6\,\text{L s}^{-1}\,\text{cm}^{-2}$$

$$A \quad = \frac{\pi d^2}{4} = 81.7\,\text{cm}^2$$

$$Pr \quad = \left(1 + \frac{3}{4}\frac{l}{d}\right)^{-1} \xi^{-1}$$

For the tube:

$$l/r \cong \frac{20}{5} \cong 4$$

From Figure 2.2, $\xi = 1.12$:

$$\therefore \quad C_{\text{tube}} = 948 \times \frac{1}{\left(1 + \frac{3}{4}\frac{20}{10.2}\right) \cdot 1.12}$$

$$= 343\,\text{L s}^{-1}$$

$$\therefore \quad \frac{1}{S_{\text{eff}}} = \frac{1}{S_0} + \frac{1}{343}$$

Here

$$S_0 = 200\,\text{L s}^{-1}$$

$$\therefore \quad S_{\text{eff}} \underline{= 126\,\text{L s}^{-1}}$$

2.5 KNUDSEN (INTERMEDIATE) FLOW THROUGH A TUBE

The region of Knudsen flow is characterised by *Kn* values between 10^{-2} and 0.5.

For long tubes of uniform circular cross-section, the equation for the pV-throughput obtained by Knudsen is given (ref. (d′)) as:

$$q_{pV} = \frac{\pi}{128}\frac{d^4}{\eta l}\frac{(p_1^2 - p_2^2)}{2} + \frac{1}{6}\sqrt{\frac{2\pi RT}{M}}\frac{d^3}{l}\frac{1 + \sqrt{\frac{M}{RT}} \cdot \frac{d}{\eta} \cdot \frac{(p_1 + p_2)}{2}}{1 + 1.24\sqrt{\frac{M}{RT}} \cdot \frac{d}{\eta}\frac{(p_1 + p_2)}{2}}(p_1 - p_2) \qquad (2.39)$$

where l and d are the length and diameter of the tube in cm, p_1 and p_2 are the entrance and exit pressures in mbar, η is the gas viscosity and M is the relative molar mass (in kg .kmol^{-1}).

For air at 20 °C:

$$q_{pV} = \left(135\frac{d^4}{l}\bar{p} + 12.1\frac{d^3}{l}\frac{1 + 189\bar{p}d}{1 + 235\bar{p}d}\right)(p_1 - p_2)\,\text{mbar L s}^{-1} \qquad (2.40)$$

where d and l are in cm and p in mbar.

Equation (2.39) can also be written in the form:

$$C_{\text{tube,Kn}} = 12.1\frac{d^3}{l}\,f\,(\bar{p}d)\,\text{L s}^{-1} \qquad (2.41)$$

$$C_{\text{tube,Kn}} = C_{\text{tube,molec.}} \times f\,(\bar{p}d) \qquad (2.42)$$

where

$$f\,(\bar{p}d) = \frac{1 + 200\bar{p}d + 2620\bar{p}^2d^2}{1 + 235\bar{p}d}$$

for

C_{tube} in L s^{-1}, d and l in cm, and p in mbar.

If $\bar{p} \times d$ is $< 10^{-2}$ mbar cm, $f\,(\bar{p}d) \rightarrow 1$

If $\bar{p} \times d$ is > 1 mbar cm, $f\,(\bar{p}d) = 0.85 + 11.15\bar{p}d$

For intermediate values, the full expression of Equation (2.41) must be used. A plot of $f\,(\bar{p}d)$ vs $\bar{p}d$ is shown in Figure 2.4 which can be used in Equation (2.41) to find conductance values.

Example 2.14

In a system used for studying reactive intermediates produced by microwave discharge, reactants are pumped through the discharge region *via* a

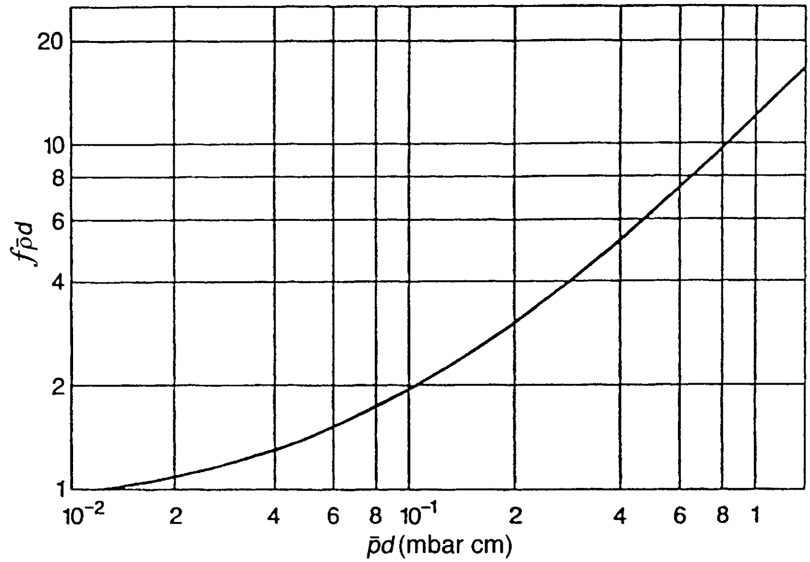


Figure 2.4 *Variation of the function f ($\bar{p}d$) with ($\bar{p}d$) for air at 20 °C*
(Reproduced from ref (d′) with permission)

tube (d = 12 mm, l = 25 cm) at a sample pressure of 0.1 mbar, to the detection region which is maintained at a much lower pressure. Calculate the transit time through the tube.

Assume that the mean pressure ($\bar{p}$) in the tube is 0.05 mbar.
From (Table 1.2):

$$\bar{l}p_{\text{air},20\,°\text{C}} = 6.5 \times 10^{-3}\,\text{cm mbar}$$

$$\bar{l} = 0.13\,\text{cm}$$

$$\therefore\quad \frac{\bar{l}}{\text{d}} = \frac{0.13\,\text{cm}}{1.2\,\text{cm}} = 0.11$$

∴ Knudsen flow is established (see Table 1.4)

From (2.42):

$$C_{\text{tube,Kn}} = C_{\text{tube,molec}} \times f\,(\bar{p}d)$$

From (2.37):

$$C_{\text{tube,molec}} = \frac{12.1d^3}{l}\,\text{L s}^{-1}$$
$$= 0.84\,\text{L s}^{-1}$$

$f(\bar{p}d)$ can be obtained from Figure 2.4 with $(\bar{p}d) = 6 \times 10^{-2}$ mbar cm giving $f(\bar{p}d) \cong 1.5$

$$\therefore \quad C_{\text{tube,Kn}} = 0.84 \times 1.5 \text{ L s}^{-1} \\ = 1.26 \text{ L s}^{-1}$$

From Equation (2.6):

$$q_{pV} = C_{\text{tube,Kn}} \times \Delta p \\ \underline{\sim 0.13 \text{ mbar L s}^{-1}}$$

At 0.05 mbar, rate of flow = $2.6 \text{ L s}^{-1} = 2600 \text{ cm}^3 \text{ s}^{-1}$

$$\therefore \quad \text{Flow velocity} = \frac{2600 \text{ cm}^3 \text{ s}^{-1}}{A_{\text{tube}} \text{ cm}^2} = \frac{2600}{1.13} \text{ cm s}^{-1} \\ = 2300 \text{ cm s}^{-1}$$

$$\therefore \quad \text{Time for 25 cm} = \underline{11 \text{ ms}}$$

Example 2.15

A right-angled, bellows-sealed DN250 ISO-K valve has a molecular flow conductance for air of 2700 L s^{-1}. Calculate its conductance for Ar. If a mean pressure of Ar of 5×10^{-3} mbar is established in the elbow, what is the conductance?

$$C_{\text{tube,air}} = 2700 \text{ L s}^{-1}$$

From Equation (2.38):

$$C_{\text{valve,Ar}} = C_{\text{valve,air}} \times \left(\frac{M_{\text{air}}}{M_{\text{Ar}}}\right)^{1/2}$$

$$C_{\text{valve,Ar}} = 2700 \times \sqrt{\frac{29}{40}} \text{ L s}^{-1}$$

$$\underline{= 2299 \text{ L s}^{-1}}$$

With $\bar{p}$ in valve = 5×10^{-3} mbar, $\bar{l}$ can be calculated.

$$\bar{l}p_{\text{Ar,20 °C}} = 6.8 \times 10^{-3} \text{ cm mbar}$$

$$\bar{l} = 1.36 \text{ cm}$$

$$Kn = \bar{l}/d = 0.05$$

This indicates that Knudsen flow is established in the valve, so from Equation (2.42):

$$C_{\text{valve,Kn}} = C_{\text{valve,molec.}} \times f\,(\bar{p}d)$$

From Figure 2.4, for $(\bar{p}d) = 0.13$ mbar cm, $f\,(\bar{p}d) \cong 2.1$:

$$\begin{aligned} C_{\text{valve,Kn,air}} &= 2700\ \text{L s}^{-1} \times 2.1 \\ &= 5670\ \text{L s}^{-1} \end{aligned}$$

$$\begin{aligned} \therefore \quad C_{\text{valve,Kn,Ar}} &= 5670 \times \sqrt{\frac{29}{40}} \\ &= \underline{4828\ \text{L s}^{-1}} \end{aligned}$$

CHAPTER 3

Pumps and Pumping Systems

3.1 INTRODUCTION

Vacuum pumps, either singly or, more usually, as part of a pumping system, create and maintain the conditions appropriate to a required process. Each of the types of vacuum pump available has a characteristic working range in which it is effective. Outside that range, shortcomings in performance become apparent.

In this chapter, those pumps that are frequently encountered throughout the range of vacuum pressures are dealt with (see Table 3.1). Where necessary, to support the calculations, the operating principles and pump characteristics are reviewed. With gas-transfer pumps operating in the HV/UHV range (typically diffusion or turbomolecular pumps), continuous operation of backing (forevacuum) pumps is required for efficient performance. In such cases, the combination is considered.

Important characteristics of vacuum pumps include the ultimate pressure (p_{ult}), the inlet pumping speed (S_0) and the variation of the latter with pressure. The type of pump or combination of pumps chosen for an application depends on the gas load to be handled and the base pressure to be achieved in a given time. Other important factors include the cleanliness of the pumping system and, with some systems, the absence or otherwise of vibrations.

An accepted criterion for cleanliness in a vacuum system depends on analysis of the residual gases it contains. A system is clean if:

$$\Sigma\, p_{i,M} \leq 1\%\, p_{\text{tot}}$$

where $M > 40$ (but excluding $M = 44$ (CO_2)), $p_{i,M}$ is the partial pressure of fragments of mass-to-charge ratio M and p_{tot} is the total pressure in the system.

Table 3.1 *Pressure ranges for vacuum pumps for chemical applications*

Pressure range (mbar)	*Pump type*
10^{+3} to 10^{-3}	Oil-sealed rotary pumps
	Rotary vane/rotary piston pumps
	1-stage, $p_{\text{ult}} \sim 10^{-1}$ mbar
	2-stage, $p_{\text{ult}} \sim 10^{-3}$ mbar
	Dry pumps
	Piston pumps, $p_{\text{ult}} \sim 1\text{–}3 \times 10^{-2}$ mbar
	Diaphragm pumps
	1-stage, $p_{\text{ult}} \sim 100$ mbar
	2-stage, $p_{\text{ult}} \sim 8$ mbar
	Hook-and-claw and related pumps
	$p_{\text{ult}} \sim 3\text{–}8 \times 10^{-1}$ mbar
	Liquid ring pumps + gas ejectors[a]
	$p_{\text{ult}} \sim$ few mbar
10^{-3} to 10^{-8}	Diffusion pumps[b,c]
	Turbomolecular pumps[b,c]
10^{-8} to 10^{-13}	Cryopumps (cryopanels)
	Turbomolecular pumps[c]
	Diffusion pumps[c,d]
	Sputter ion pumps
	Getter pumps
	Evaporable (titanium sublimation)
	Non-evaporable

[a] For high gas throughputs at low pressures, Roots pumps can be used to boost their performance, as long as $S_{\text{Roots}}/S_{\text{backing}}$ is acceptable (see Section 3.2.3).

[b] In certain applications such pumps are usually used in combination with cryosurfaces at −100 °C to −196 °C to enhance the pumping speed for water vapour.

[c] Used in combination with suitable backing pumps.

[d] Rarely used.

3.2 VACUUM PUMPS (ROUGH–MEDIUM VACUUM RANGE)

3.2.1 Oil-sealed Rotary Pumps

Such pumps are gas-transfer pumps. They are used extensively both to back high-vacuum pumps and to act as devices for achieving pressures in the rough–medium range in activities such as distillation, drying, *etc.*

The role of the oil in these pumps is to seal (isolate low pressure gas entering *via* the inlet from higher pressure gas at the outlet), lubricate and transfer heat. It also allows high degrees of gas compression to be achieved.

For gas-transfer pumps generally, the compression ratio (k) can be defined as:

$$k = \frac{p_{\text{outlet}}}{p_{\text{inlet}}} \tag{3.1}$$

With oil-sealed rotary pumps, it is possible to achieve values of k of 10^5 to 10^6.

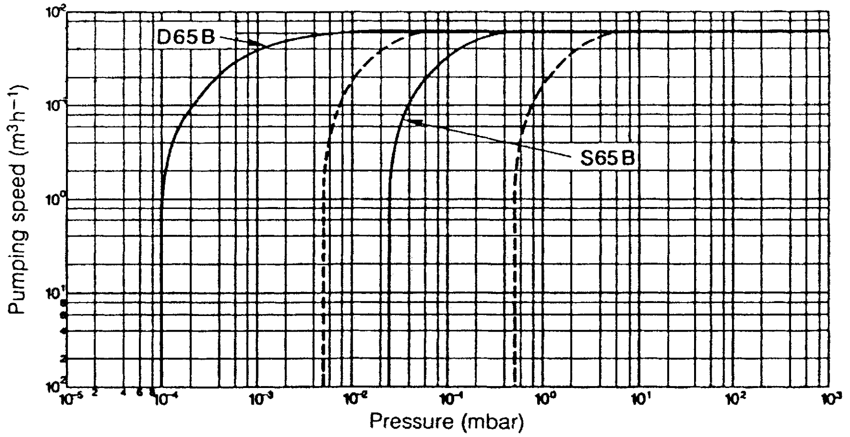


Figure 3.1 *Pumping speed (volume rate of flow) as a function of pressure ($S_0 = 65\,m^2\,h^{-1}$) for single-stage (S-) and two-stage (D-) rotary vane pumps:* —— *without gas ballast;* ----- *with gas ballast*
(Manufacturer's data for S65B/S65B rotary vane pumps manufactured by Leybold Vakuum GmbH)

The S_0 vs p characteristics of typical single- and two-stage oil-sealed rotary pumps are shown in Figure 3.1. For the single-stage pump, S_0 is almost constant from atmospheric pressure down to about 1 mbar. At lower pressures, the pumping speed decreases with increasing rapidity until the ultimate pressure (p_{ult}) is reached where $S_0 = 0$. Generally, p_{ult} for a single-stage pump is about 10^{-1} mbar; 10^{-2} mbar could only be achieved by placing a cold trap between the pump and the vacuum gauge to condense oil/water vapour. With two-stage pumps, S_0 is constant down to 10^{-2} mbar before it begins to decrease. Such pumps, with cold traps, will achieve $p_{\text{ult}} = 10^{-4}$ mbar.

Oil-sealed pumps are sources of potential problems in vacuum systems. Misused, or inadequately trapped, they can cause significant contamination of high vacuum (HV) and ultra-high vacuum (UHV) systems (Figure 3.2). In systems containing reactive gases and/or abrasive particles, the pump fluid is highly susceptible to attack or change unless carefully selected and protected by efficient filters and barrier gases. Further, because of the high degree of gas compression, oil-sealed pumps cannot deal with certain vapours (*e.g.* water, ethanol) which may condense in the pump during compression.

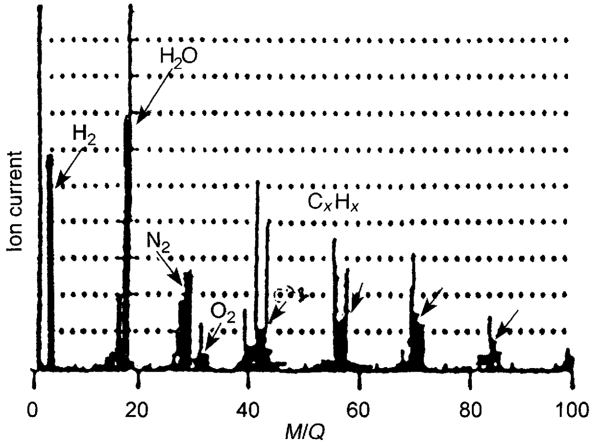
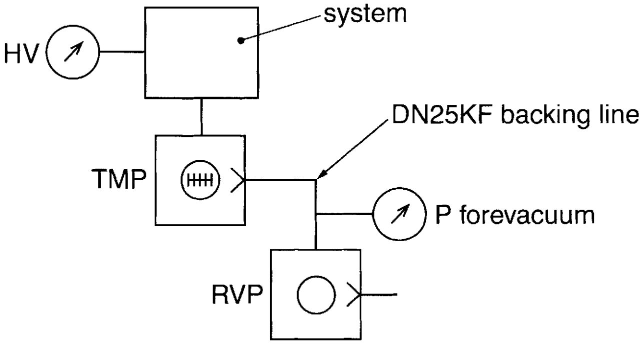


Figure 3.2 *RGA of components at the inlet of an oil-sealed rotary pump contaminated with pump oil. Masses 28*, 41 and 43, 55 and 57, 67 and 69 etc. are due to hydrocarbon fragments occurring at mass intervals 14 (–CH_2–); *Mass 28 is frequently due to N_2 from air-in-leakage*

Example 3.1

A two-stage, oil-sealed rotary vane pump is used to back a turbo-molecular pump *via* a DN25KF line (see below). Under normal working conditions, the pressure in the backing line is (2 to 6) × 10^{-3} mbar. Would the TMP become contaminated by the backing pump?



In this case, if it is assumed that the $\bar{l}p$ values at 293 K of such fragments (Figure 3.2) can be calculated using Equation 1.21 with d (collision cross-section radius) at 4×10^{-10} m (see values for $M = 40$, 44 in Table 1.1), then $\bar{l}p = 5.69 \times 10^{-3}$ Pa m.

Therefore:

$$\text{at } 2 \times 10^{-3}\,\text{mbar}, \bar{l} \cong 3\,\text{cm}$$
$$\text{at } 6 \times 10^{-3}\,\text{mbar}, \bar{l} \cong 1\,\text{cm}$$

As the diameter of the backing line is close to $\bar{l}$, certainly at the lower pressure, oil-backstreaming is a possibility.

Since the fully accelerated TMP will have a high compression ratio for mass fragments with $M > 40$ (see Section 3.3.2), this may be of little consequence if the TMP runs continuously. If, however, the TMP is operated intermittently, contamination could be a problem.

If contamination is undesirable then the following precautions can be taken:

- gas can be admitted to the backing line so that $p_{\text{back}} \cong 10^{-1}$ mbar. This value would be close to the operating limit of a classic TMP;
- an adsorption trap (activated Al_2O_3) can be fitted to the backing line. Maintenance of this trap is then necessary.
- a trap incorporating a heated combustion catalyst can be fitted.

Condensation of vapours can cause severe problems with oil-sealed pumps. By the use of gas ballast (a continuous, controlled admission of air or inert gas to the pump), this can be significantly reduced. The gas ballast increases the pressure in the pump chamber to 100 mbar just before compression starts. The compression ratio k is thereby reduced to ~10 to 15:1, and vapours which might otherwise have condensed may remain in the vapour phase.

The amount of gas ballast (GB) required is given below:

$$q_{pV,\text{ballast}} = S_0 \frac{p_{\text{vap},1}}{p_s} \left[p_{\text{ex}} - p_s \left(1 + \frac{p_1}{p_{\text{vap},1}} \right) \right] \tag{3.2}$$

where $q_{pV,\text{ballast}}$ = amount of ballast entering the pump (usually $\cong 0.1\, S_0 \times p_0$ (see manufacturer's data)) where S_0 = inlet pumping speed of the pump in L s^{-1})

p_0 = atmospheric pressure (or the pressure of other gas at the GB inlet if inert gas is being admitted)

$p_{\text{vap},1}$ = pressure of vapour in the mixture to be pumped

p_s = saturated vapour pressure of the vapour being pumped at the temperature of the coolest part of the pump (usually the exhaust). For a 'warmed-up' pump, this temperature can range from 60 °C to 70 °C.

p_{ex} = the pressure at the pump exhaust (~ 1.1 to 1.3 bar increasing to about 1.5 bar for pumps with exhaust filters)

p_1 = the pressure of non-condensable gas at the inlet

The presence of a permanent (non-condensable) gas load together with the condensable vapour means that a smaller amount of gas ballast is required to pump vapour. The worst situation arises when no permanent gas is initially present. Under such conditions, from Equation (3.2):

$$q_{pV,\text{ballast}} = S_0 \frac{p_{\text{vap},1}}{p_\text{s}} (p_\text{ex} - p_\text{s}) \tag{3.3}$$

The maximum pressure of vapour that a vacuum pump, under ambient conditions of $T = 20\,°\text{C}$, $p = 1013\,\text{mbar}$, can take in and transport is called the *vapour tolerance* of the pump. Since water vapour is the most commonly encountered vapour, pump manufacturers usually quote the 'water vapour tolerance' for their pumps. The vapour tolerance can be obtained by rearrangement of Equation (3.3):

$$p_{\text{vap},1} = \frac{0.1\ S_0 \times p_0}{S_0} \times \frac{p_\text{s}}{(p_\text{ex} - p_\text{s})} \tag{3.4}$$

where $p_{\text{vap},1}$ = vapour tolerance if no permanent gas is initially present.

Where water is the vapour to be pumped, the water vapour entering with the ballast air has to be accounted for and so Equation (3.4) becomes:

$$\text{water vapour tolerance} = 0.1 p_0 \times \frac{(p_\text{s} - p_\text{w,a})}{(p_\text{cx} - p_\text{s})} \tag{3.5}$$

where $p_\text{w,a}$ = the partial pressure of water vapour in the ballast air.

Table 3.2 lists values for p_s of water vapour over a range of temperatures.

Table 3.2 *Saturated vapour pressure* (p_s) *for water over a range of temperatures*

T(°C)	p_s(mbar)
0	6.1
20	23.4
30	42.4
60	199.2
65	250.1
70	311.6
75	385.5

Reproduced from ref. (e).

Example 3.2

A two-stage oil-sealed rotary vane pump ($S_0 = 65\,\mathrm{m^3/h}$) has achieved its normal running temperature.

(a) If the exhaust temperature is 70 °C and dry air is used as the ballast gas, calculate the water vapour tolerance if $p_0 = 1013\,\mathrm{mbar}$.

(b) If the ballast gas is atmospheric air at 20 °C and Relative Humidity (RH) = 50%, calculate the water vapour tolerance.

(a) From Equation (3.5) and Table 3.2:

$$\text{Water vapour tolerance} = 0.1p_0\left(\frac{311.6}{p_{\mathrm{ex}} - 311.6}\right)\mathrm{mbar}$$

If there are no exhaust filters, then assume $p_{\mathrm{ex}} = 1100\,\mathrm{mbar}$

$$\therefore \quad \text{water vapour tolerance} = 0.1 \times 1013 \times \left(\frac{311.6}{1100 - 311.6}\right)\mathrm{mbar}$$

$$\underline{= 40\,\mathrm{mbar}}$$

(b) From Table 3.2, the partial pressure of water vapour at 20 °C and RH = 50% is 11.7 mbar.

$$\text{Water vapour tolerance} = 0.1p_0\left(\frac{312 - 11.7}{1100 - 312}\right)$$

$$\underline{= 38.6\,\mathrm{mbar}}$$

Example 3.3

A single-stage rotary vane pump ($S_0 = 25\,\mathrm{m^3\,h^{-1}}$) is used to remove residual water from a vacuum vessel which has been cleaned, washed with demineralised water and drained. The pump is fitted with an oil-mist filter. If the exhaust temperature is 75 °C and ambient air ($T = 20\,°\mathrm{C}$, RH = 50%, $p_0 = 1013\,\mathrm{mbar}$) is used as the ballast gas, calculate the maximum amount of water that can be handled by the pump. (Assume that the pump is directly connected to the chamber.)

Assume $p_{\mathrm{ex}} = 1400\,\mathrm{mbar}$

$p_{\mathrm{s,\ water,\ 75\,°C}} = 385.5\,\mathrm{mbar}$

From Equation (3.5):

$$\text{water vapour tolerance} = 0.1p_0\left(\frac{385.5 - 11.7}{1400 - 385.5}\right)\mathrm{mbar}$$
$$= 37.3\,\mathrm{mbar}$$

The maximum amount of water that can be handled:

$$\begin{aligned}(q_{pV,\mathrm{H_2O,max}} &= S_{\mathrm{eff}} \times \text{water vapour tolerance})\\ &= S_0(\mathrm{m^3\,h^{-1}}) \times \text{water vapour tolerance (mbar)}\\ &= \frac{25}{3.6}\,\mathrm{L\,s^{-1}} \times 37.3\,\mathrm{mbar}\\ &= 259.0\,\mathrm{mbar\,L\,s^{-1}}\end{aligned}$$

From Equation (2.4): $$p\dot{V} = \frac{\dot{m}}{M}\mathrm{RT}$$

$$\begin{aligned}\therefore\quad \dot{m} &= \frac{257\,\mathrm{mbar\,L\,s^{-1}} \times 18\,\mathrm{g\,gmol^{-1}}}{83.14\,\mathrm{mbar\,L\,mol^{-1}\,K^{-1}} \times 348\,\mathrm{K}}\\ &= 0.16\,\mathrm{g\,s^{-1}}\\ &= \underline{0.58\,\mathrm{kg\,h^{-1}}}\end{aligned}$$

Example 3.4

Ethanol is to be pumped with an oil-sealed rotary pump with an exhaust pressure of 1.3 bar. Calculate the vapour tolerance to ethanol if the pump temperature is about 60 °C and atmospheric pressure is 1000 mbar.

Table 3.3 *Saturated vapour pressures* (p_s) *for some organic compounds over a range of temperatures*

	p_s (mbar)					
Substance/T °*C*	5	20	25	50	100	500
1,4-Dioxan	−17.2	−6.1		23.9	38.6	79.9
Ethanol	−15.7	−6.4	7	17.9	29.7	62
Isopropanol	−10.6	−1.6	11.7	22.7	34.4	66.4
Methanol	−28.9	−20.1	−7.0	3.9	15.9	48.4
Toluene	−8.7	−1.8	17.2	30.5	45.3	87.5

From Table 3.3 ethanol has a saturated vapour pressure p_s of 500mbar at 62 °C (~60 °C). From Equation (3.4):

$$\begin{aligned}\text{ethanol tolerance} &= 0.1p_0\left(\frac{p_\mathrm{s}}{p_\mathrm{ex} - p_\mathrm{s}}\right)\\ &= \underline{63\,\mathrm{mbar}}\end{aligned}$$

In the absence of gas ballast, the likelihood of condensation occurring is significant unless a permanent (non-condensable) gas is present. The ratio $p_{\text{vap,l}}/p_\text{l}$ can be obtained from Equation (3.2) with $q_{pV,\text{ballast}} = 0$. Rearrangement gives:

$$\frac{p_{\text{vap,l}}}{p_\text{l}} = \left(\frac{p_\text{ex}}{p_\text{s}} - 1\right)^{-1} \tag{3.6}$$

by inserting relevant values of p_ex and p_s, the critical ratio $p_{\text{vap,l}}/p_\text{l}$ can be calculated.

Example 3.5

A mixture of water vapour and air is to be removed from a vessel using an oil-sealed rotary pump. If the exhaust temperature is 65 °C and the pump is not fitted with an exhaust filter, calculate the critical partial pressure ratio which should not be exceeded if condensation is to be prevented.

The pressure ratio is given by Equation (3.6).

Taking $p_\text{s} = 250.1$ mbar, $p_\text{ex} = 1.3$ bar, then:

$$\frac{p_\text{vap}}{p_\text{air}} = \left(\frac{1300}{250} - 1\right)^{-1}$$

$$= 0.24$$

$$\therefore \quad \underline{\frac{p_\text{vap}}{p_\text{tot}} = 0.19}$$

This indicates that the vapour pressure of the water should be less than 19% of the total pressure and less than 24% of the permanent gas (air) pressure.

Example 3.6

A turbomolecular pump ($S_{\text{N}_2} = 1150\,\text{L}\,\text{s}^{-1}$ at 10^{-3} mbar) is fitted with a purge gas inlet that directs 36 sccm N_2 into the TMP to protect the bearings and motor housing. The purge gas passes to the backing line. If the TMP requires a backing pressure of 10^{-1} mbar, calculate the size and type of backing pump if purge gas is being admitted and (a) the TMP is working at $p_\text{in} \leq 10^{-3}$ mbar, (b) it is maintaining 10^{-2} mbar ($S_\text{TMP} = 700\,\text{L}\,\text{s}^{-1}$).

(a) If the TMP has $p_\text{in} \leq 10^{-3}$ mbar, the maximum throughput will be obtained at 10^{-3} mbar.

$$\begin{aligned} \therefore \quad q_{pV,\mathrm{TMP}} &= 1150\,\mathrm{L\,s^{-1}} \times 10^{-3}\,\mathrm{mbar} \\ &= 1.15\,\mathrm{mbar\,L\,s^{-1}} \end{aligned}$$

$$\begin{aligned} q_{pV,\mathrm{purge}} &= 36\,\mathrm{sccm\ N_2} \\ &= \frac{36\,\mathrm{cm^3} \times 1013\,\mathrm{mbar}}{10^3 \times 60\,\mathrm{s}} = 0.61\,\mathrm{mbar\,L\,s^{-1}} \end{aligned}$$

$$\begin{aligned} \therefore \quad q_{pV,\mathrm{tot}} &= (1.15 + 0.61)\,\mathrm{mbar\,L\,s^{-1}} \\ &= 1.76\,\mathrm{mbar\,L\,s^{-1}} \end{aligned}$$

which must be handled by the backing pump at 10^{-1} mbar. The minimum speed (S_{min}) of this pump is given by:

$$\begin{aligned} S_{\mathrm{min}} &= \frac{q_{pV,\mathrm{tot}}}{p_{\mathrm{back}}} = \frac{1.76\,\mathrm{mbar\,L\,s^{-1}}}{10^{-1}\,\mathrm{mbar}} \\ &= \underline{17.6\,\mathrm{L\,s^{-1}} (\cong 63\,\mathrm{m^3\,h^{-1}})} \end{aligned}$$

This pumping speed is achievable using a two-stage oil-sealed rotary pump. If a dry pump, such as a hook-and-claw pump is required, then a Roots + dry pump combination would have to be used because of the limited p_{ult} of the dry pump (see Figure 3.3).

(b) At 10^{-2} mbar, $S_{\mathrm{TMP}} = 700\,\mathrm{L\,s^{-1}}$

$$\therefore \quad q_{pV,\mathrm{TMP}} = 7\,\mathrm{mbar\,L\,s^{-1}}$$

As $q_{pV,\mathrm{purge}} = 0.61\,\mathrm{mbar\,L\,s^{-1}}$

$$q_{pV,\mathrm{tot}} = \underline{7.61\,\mathrm{mbar\,L\,s^{-1}}}$$

To maintain 10^{-1} mbar, S_{min} for the backing pump should be $76.1\,\mathrm{L\,s^{-1}}$ ($\sim 275\,\mathrm{m^3\,h^{-1}}$). This is achievable with, say, a Roots + two-stage oil-sealed rotary pump combination *e.g.* $S_{\mathrm{Roots}} = 500\,\mathrm{m^3\,h^{-1}}$, $S_{\mathrm{rotary}} = 60\,\mathrm{m^3\,h^{-1}}$.

3.2.2 Dry Pumps

Because of the problems that can potentially arise with oil-sealed pumps, there is an increasing trend to use dry pumps in many applications. Various types are available including Roots pumps backed with suitable pumps (see Section 3.2.3), multi-stage Roots pumps, screw-, hook-and-claw- and scroll pumps. Dry piston pumps and diaphragm pumps are also available but their pumping speed range is restricted. The characteristics, particularly S_0 and p_{ult}, of some types of dry pumps, and their applications are summarised in Table 3.4.

Table 3.4 *Characteristics and Applications of Dry vacuum pumps*

	Pump type				
Parameter	*Claw*	*Screw*	*Scroll*	*Piston*	*Diaphragm*
S_0 ($\text{m}^3\,\text{h}^{-1}$) range	25–100	250–2700	20–50	14 (3-stage) to 40 (2-stage)	0.6–5.0
p_{ult} (mbar)	$4\text{–}6 \times 10^{-1}$	$4\text{–}6 \times 10^{-3}$	10^{-2}	$4\text{–}6 \times 10^{-2}$	0.5–8.0
Applications	Roots backing (S_{tot} = 150–500 $\text{m}^3\,\text{h}^{-1}$) in a range of applications TMP backing Clean systems	Large-scale chemical applications	TMP backing Clean systems	Roots backing TMP backing Clean systems	Drying Distillation Rotary evaporators TMP (wide-range) backing

The pumping speed vs pressure curves for hook-and-claw pumps and a multi-stage dry piston pump are shown in Figures 3.3 and 3.4, respectively.

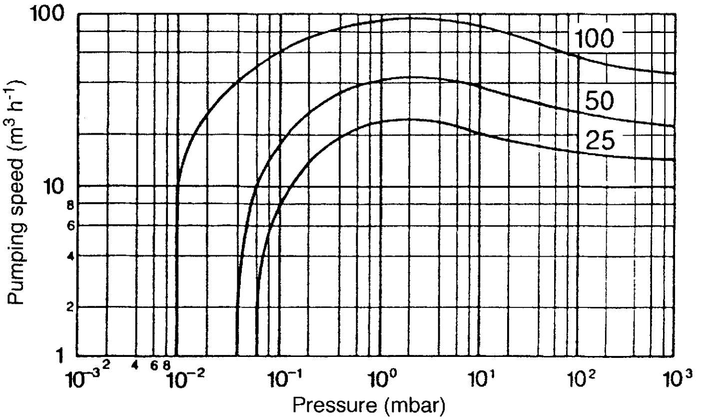


Figure 3.3 *Pumping speed curves for four-stage hook-and-claw pumps (S_{nom} = 100, 50 and 25 $m^3\,h^{-1}$) at 50Hz*

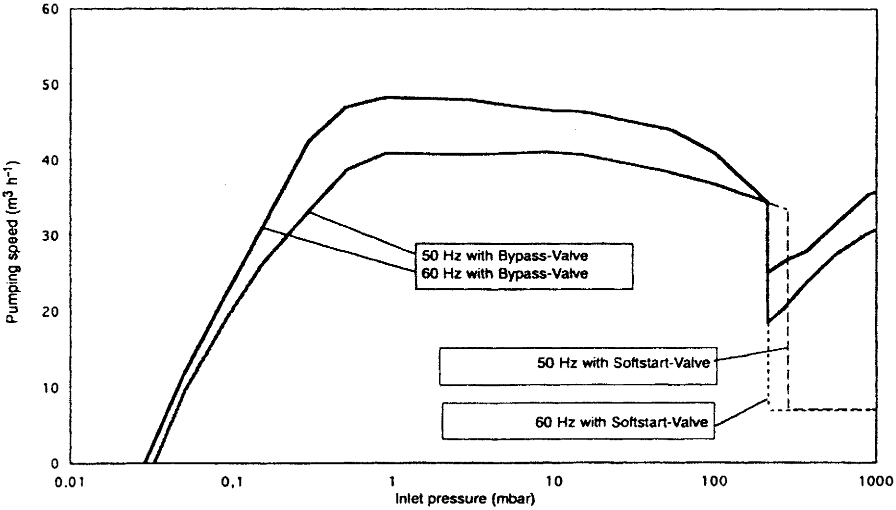


Figure 3.4 *Pumping speed characteristics of a four-stage dry piston pump* ($S_{0,max}$ = *30 (60 Hz) – 40 (50 Hz)* $m^3 h^{-1}$)

3.2.3 Roots Pumps

Roots pumps must be combined with a backing pump/pump-set for normal vacuum applications. Used in combination with any of a range of backing pumps (oil-sealed rotary, dry, liquid-ring) Roots pumps allow higher pumping speeds and lower pressures to be achieved than can be obtained by the backing pump on its own.

Selection of the backing pump is determined by the application, major factors considered being:

the required pumping speed/pressure
the nature (condensable, corrosive, *etc.*) of the gas load to be handled
the cleanliness requirements of the system.

The relative pumping speeds of the pumps ($S_{\text{Roots}}/S_{\text{back}}$) is largely determined by requirements for:

good volumetric efficiency for the combination
restriction of the pressure difference across the Roots pump (see below).

Because commercially available Roots pumps have fairly large pumping speeds (*e.g.* 250 $m^3 h^{-1}$ up to several thousand $m^3 h^{-1}$), their use in general chemistry is restricted. They are, however, appropriate for use in large-scale vacuum distillation, solvent recovery and the handling of large quantities of specific gases in, for example, He recovery and plasma-enhanced processes.

A Roots vacuum pump has two symmetrical impellers, contra-rotating (at 50 or 60 Hz) inside a housing (see Figure 3.5).

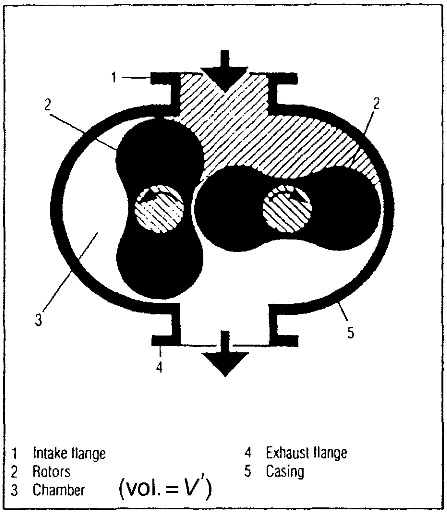


Figure 3.5 *Cross-section of a single-stage Roots pump*

There are small internal clearances (< 1 mm usually) between the rotors and the housing and between the rotors themselves. Relatively low pressures (in the medium vacuum range) can, however, be achieved. Importantly, there is no oil sealing in the gas-handling part of the pumps.

The nominal (theoretical) pumping speed (S_{th}) of a Roots pump is:

$$S_{\text{th}} = 4 \times n \times V'$$

where n = rotational speed of the rotors and V' = volume of gas isolated from inlet (Figure 3.4).

The theoretical gas throughput of a Roots pump is therefore:

$$q_{pV,th} = S_{\text{th}} \text{P}_{\text{in}} \tag{3.7}$$

Because of the clearances within a Roots pump, internal leakage can occur, reducing the amount of gas handled so that:

$$q_{pV,\text{eff}} = q_{pV,\text{th}} - q_{pV,\text{ int.leak}} \tag{3.8}$$

where $q_{pV,\text{int.leak}}$ = gas throughput due to internal leakage.

This is made up of two gas sources, so:

$$q_{pV,\text{int.leak}} = C_{\text{gap}}\,(p_{\text{out}} - p_{\text{in}}) + S_{\text{b}} \times p_{\text{out}}$$

where C_{gap} = the conductance of the internal clearances

S_{b} = volume rate of flow of gas transported by adsorption (on forevacuum side) – desorption (at inlet side) by the impellers

$(p_{\text{out}} - p_{\text{in}})$ = pressure difference across the Roots pump.

An important characteristic of a Roots pump is its k_0 value. This is the ratio of the pressures at the outlet (p_{out}) to the inlet (p_{in}) of the pump under zero throughput conditions:

$$k_0 = \left(\frac{p_{\text{out}}}{p_{\text{in}}}\right)_0 \tag{3.9}$$

k_0 for a pump depends on the shape of the rotors and the clearances between the rotors and the housing. It is found by measurement as a function of p_{out} and is usually given by the manufacturer. It is dependent on gas type. k_0 is measured by closing the inlet to the Roots pump and admitting gas between the outlet of the Roots and the inlet of the backing pump as shown in Figure 3.6. It's variation with p_{out} is shown in Figure 3.7. The internal gas transport ($q_{pV,\text{int.leak}}$) can be expressed as a function of k_0 at various p_{out} values.

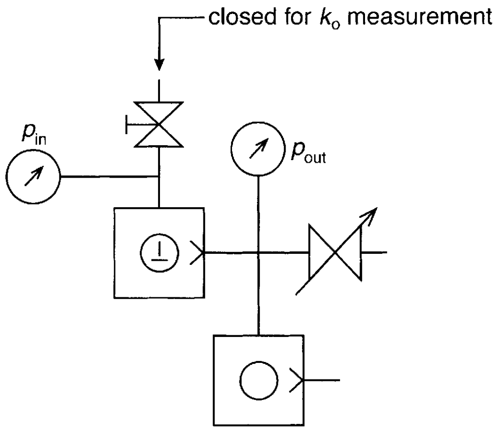


Figure 3.6 *Measurement of* k_0

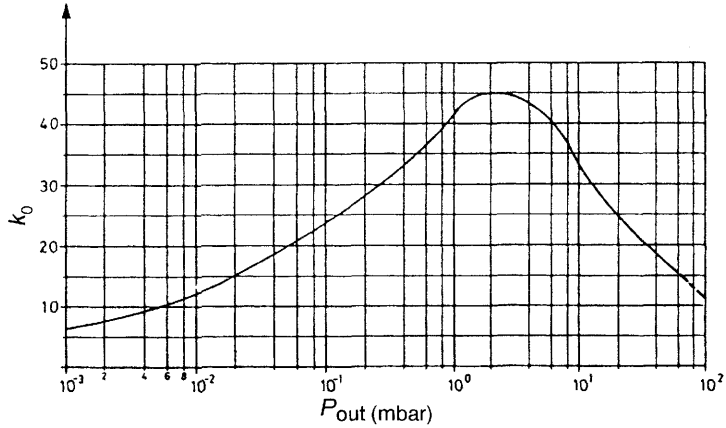


Figure 3.7 *Variation of k_0 with p_{out} for a 2000 m^3 h^{-1} Roots pump handling air*

The net pumping speed of a Roots pump is obtained from the following expression:

$$S_{eff,Roots} = S_{th} \frac{k_0(p_{out})}{k_0(p_{out}) + \dfrac{S_{th}}{S_{back}(p_{back})} - 1} \tag{3.10}$$

The mechanical efficiency of the Roots pump (*i.e.* $S_{eff,\,Roots}/S_{th}$) is given by:

$$\eta = \frac{S_{eff}}{S_{th}} = \frac{k_0}{k_0 + \dfrac{S_{th}}{S_{back}} - 1} \tag{3.11}$$

The ratio (S_{eff}/S_{back}) is known as the staging ratio or gradation.

If the pumping speed vs pressure characteristic of a Roots pump + backing pump is required, the calculation starts by assuming values for p_{out} and obtaining values of S_{back} corresponding to p_{out} from S_{back} *vs* p curves (usually provided by the manufacturer of the backing pump) where in this case, $p = p_{out}$.

The staging ratio can then be obtained from S_{back} values and k_0 from the manufacturer's data.

The volumetric efficiency of the Roots pump is thus determined, leading to S_{eff}. As:

$$p_{in}S_{eff} = p_{out}S_{back}$$

then
$$p_{\text{in}} = p_{\text{out}} \frac{S_{\text{back}}(p_{\text{out}})}{S_{\text{eff}}} \tag{3.12}$$

where $S_{\text{back}}(p_{\text{out}})$ indicates that S_{back} is a function of p_{out} and therefore needs to be obtained as above.

Roots efficiencies of about 70% or more can be achieved if $k_0 \geq 20$ and $S_{\text{th}}/S_{\text{back}} \leq 10$. Although such values for the staging ratio are satisfactory in the medium vacuum range, lower values are desirable if there are large variations in operating pressures or if the Roots pump is working where k_0 is small.

The ultimate pressure of a Roots blower/backing pump combination is approximately that of the backing pump divided by the compression ratio (k_0) for the Roots pump at this pressure. In practice, however, the calculated value should be multiplied by a factor of 4 to 5 to take into account performance deficiencies of the backing pump.

Relatively high compression ratios can be achieved with Roots pumps at high vacuum pressures but there is a maximum pressure difference (Δp_{max}) at which they can be satisfactorily operated. This is determined predominantly by the temperature rise of the gas at the exhaust of the pump. Pump manufacturers specify Δp_{max} in their data for Roots pumps and it refers to continuous operation of a pump with no additional control features such as by-pass valves and similar devices.

To prevent overheating, such pumps are usually switched on using pressure switches and Δp_{max} determines the pressure at which the Roots pump can be switched on:

$$p_{\text{switch on}} = \frac{\Delta p_{\text{max}}}{\eta \frac{S_{\text{th}}}{S_{\text{back}}} - 1} \tag{3.13}$$

A safe value for the cut-in pressure can be calculated using $k_0 = 15$ (ref. W. Schwartz, p. 507 in ref. (f)).

Example 3.7

A Roots vacuum pump with a theoretical pumping speed (S_{th}) of $500\,\text{m}^3\,\text{h}^{-1}$ is backed by a dry pump designed for the chemical industry. Under working conditions, the dry pump has a speed of $50\,\text{m}^3\,\text{h}^{-1}$.

(a) What is the effective speed of the Roots pump when k_0 is 20?
(b) What are the inlet and backing pressures if a gas flow of $20\,\text{mbar L s}^{-1}$ is handled?

(a) From Equation (3.11)

$$S_{\mathrm{eff}} = \eta S_{\mathrm{th}} = \left(\frac{k_0}{k_0 + \dfrac{S_{\mathrm{th}}}{S_{\mathrm{back}}} - 1} \right) S_{\mathrm{th}}$$

With $k_0 = 20$, $S_{\mathrm{th}} = 500\,\mathrm{m^3\,h^{-1}}$ and $S_{\mathrm{back}} = 50\,\mathrm{m^3\,h^{-1}}$:

$$\eta = 0.69\ (69\%)$$

$$\therefore\quad S_{\mathrm{eff}} \underline{= 345\,\mathrm{m^3\,h^{-1}}\ (95.8\,\mathrm{L\,s^{-1}})}$$

(b) With $q_{pV} = 20\,\mathrm{mbar\,L\,s^{-1}}$ and $S_{\mathrm{eff}} = 95.8\,\mathrm{L\,s^{-1}}$:

$$p_{\mathrm{in}} = \frac{20\,\mathrm{mbar\,L\,s^{-1}}}{95.8\,\mathrm{L\,s^{-1}}}$$

$$\underline{= 0.21\,\mathrm{mbar}}$$

$$p_{\mathrm{out}} = \frac{20\mathrm{mbar\,L\,s^{-1}}}{S_{\mathrm{back}}\,\mathrm{L\,s^{-1}}}$$

$$= \frac{20\,\mathrm{mbar\,L\,s^{-1}}}{13.9\,\mathrm{L\,s^{-1}}}$$

$$\underline{= 1.4\,\mathrm{mbar}}$$

Example 3.8

A Roots pump ($S_{\mathrm{th}} = 150\,\mathrm{m^3\,h^{-1}}$) is backed by a directly connected dry piston pump. Calculate the pumping speed of the combination given the data in Tables 3.5 and 3.6, provided by the manufacturer.

Table 3.5 *Pumping speed* (S_0) *vs pressure for the dry piston pump*

p *(mbar)*	S_0 *($m^3\,h^{-1}$)*
20	39
10	40
5	40
1	40
0.5	35
0.1	20
0.08	16
0.06	13

Table 3.6 k_0 *values for the Roots pump*

p_{back} *(mbar)*	k_0
20	15
10	22
5	30
1	39
0.5	35
0.1	20
0.08	18
0.06	18

$$S_{\text{eff, Roots}} = \eta \times S_{\text{th}}$$

$$\eta = \frac{k_0}{k_0 + \dfrac{S_{\text{th}}}{S_{\text{back}}} - 1}$$

Tabulating the above data:

p_{back} *(mbar)*	*Dry pump* $S_0 (m^3 h^{-1})$	S_{th}/S_{back}	k_0 *at* p_{back}	η	$S_{eff} = \eta S_{th}$ $(m^3 h^{-1})$
20	39	3.9	15	0.84	126
10	40	3.75	22	0.89	134
5	40	3.75	30	0.92	138
1	40	3.75	39	0.93	140
0.5	35	4.3	35	0.91	137
0.1	20	7.5	20	0.76	114
0.08	16	9.4	18	0.68	102
0.06	13	11.5	18	0.63	95

From the continuity equation:

$$p_{\text{in}} \times S_{\text{eff,Roots}} = p_{\text{back}} \times S_{\text{0,dry}}$$

$$\therefore \quad p_{\text{in}} = p_{\text{back}} \times \frac{S_{\text{0,dry}}}{S_{\text{eff,Roots}}}$$

An additional Table can be drawn up showing p_{in} for the Roots pump and the corresponding S_{eff}:

p_{back} (mbar)	$S_{eff,Roots}$ ($m^3 h^{-1}$)	$S_{0,dry}$ ($m^3 h^{-1}$)	p_{in} (mbar)
20	126	39	6.2
10	134	40	3.0
5	138	40	1.5
1	140	40	0.29
0.5	137	35	0.13
0.1	114	20	0.018
0.08	102	16	0.013
0.06	95	13	8×10^{-3}

Note: In this example, $S_{\mathrm{eff,Roots}}$ represents the pumping speed at the entrance to the Roots pump. Additional connections to the system will further reduce $S_{\mathrm{eff,Roots}}$ because of conductance losses.

Example 3.9

It is proposed to use a distillation system working at about 5 mbar to separate thermally sensitive material from crude process material. The distillation system is to be evacuated with a Roots pump ($S_{\mathrm{th}} = 500\,\mathrm{m^3\,h^{-1}}$) connected to a dry backing pump with a pumping speed of $200\,\mathrm{m^3\,h^{-1}}$. The Roots pump is to be switched on at 50 mbar.

(a) If k_0 for the Roots pump at this pressure is 12 and, according to the manufacturer, the maximum pressure difference across the Roots pump should not exceed 80 mbar, evaluate the suitability of the proposed system (in terms of the allowable Δp_{max} and the efficiency).

(b) If the backing pump has an ultimate pressure (p_{ult}) of 8 mbar, estimate p_{ult} for the combination.

(c) Since warming of the pumped gases will occur in the Roots pump, calculate the temperature rise if the process is polytropic (see below) and the predominant gas load at 50 mbar is air at 333 K (polytropic exponent $n = 1.2$).

(a) At the proposed switch-on pressure, the efficiency of the Roots + backing pump combination is given by Equation (3.11):

$$\eta = \frac{k_0}{k_0 + \dfrac{S_{\mathrm{th,Roots}}}{S_{\mathrm{back}}} - 1}$$

$$= \frac{12}{12 + \frac{500}{200} - 1}$$

$$\underline{= 0.89 \text{ (efficiency is high (> 75\%)}}$$

$$\therefore \quad S_{\text{eff, Roots}} = 500\,\text{m}^3\,\text{h}^{-1} \times 0.89$$
$$= 444\,\text{m}^3\,\text{h}^{-1}$$

The actual pressure difference ($p_{\text{back}} - p_{\text{in}}$) can be calculated by using the continuity equation to evaluate p_{back}:

$$p_{\text{in}}\, S_{\text{eff,Roots}} = p_{\text{back}}\, S_{\text{back}}$$

$$p_{\text{back}} = \frac{50\,\text{mbar} \times 444\,\text{m}^3\,\text{h}^{-1}}{200\,\text{m}^3\,\text{h}^{-1}}$$
$$= 111\,\text{mbar}$$

$$\therefore \quad \Delta p = (111 - 50)\,\text{mbar}$$
$$= 61\text{ mbar (below manufacturer's allowable } \Delta p_{\text{max}})$$

The system has a high efficiency and will work within the limits of the Roots pump.

(b) If the backing pump has an ultimate pressure of 8 mbar, p_{ult} of the combination will be $= p_{\text{ult}}/k_{0,\text{Roots}}$ at p_{ult}.
If k_0 at 8 mbar = 26 then

$$p_{\text{ult}} = 0.31\text{ mbar}$$

In practice, this calculated value should be multiplied by a factor of (4–5) so realistically p_{ult}:

$$p_{\text{ult}} = 0.31\,\text{mbar} \times 5$$
$$\underline{= 1.5\,\text{mbar}}$$

(c) In practice, many processes take place neither isothermally (pV = constant) nor adiabatically (pV^{γ} = constant) but polytropically where they approximate to a law of the form pV^n = constant, where $1 < n < \gamma$. In positive displacement pumps, both vapours and perfect gases obey this type of law.

For any polytropic process, we can write:

$$\frac{p_1}{p_2} = \left(\frac{V_2}{V_1}\right)^{n}$$

If the gas is perfect then $pV = RT$ and, substituting $p = \frac{RT}{V}$ into pV^n = constant, we get:

$$TV^{n-1} = \text{constant}$$

or

$$\frac{T}{p^{(n-1)/n}} = \text{constant}$$

$$\therefore \quad \left(\frac{T_1}{T_2}\right) = \left(\frac{p_1}{p_2}\right)^{(n-1)/n}$$

In this case, the subscript 1 refers to Roots outlet conditions and subscript 2 refers to Roots inlet conditions.

$$\therefore \quad T_{\text{out}} = T_{\text{in}} \left(\frac{p_{\text{out}}}{p_{\text{in}}}\right)^{(n-1)/n}$$

$$\therefore \quad T_{\text{out}} = 333\,\text{K} \left(\frac{p_{\text{back}}}{p_{\text{in}}}\right)^{0.2/1.2}$$

$$= 333\,\text{K}\left(\frac{111}{50}\right)^{0.2/1.2}$$

$$= 333\,\text{K} \times 1.14$$

$$= 380\,\text{K}$$

$$\therefore \quad \underline{\Delta T = 47\,\text{K}}$$

3.3 HIGH/ULTRA-HIGH VACUUM PUMPS

It is now increasingly common to have high-vacuum systems based on turbomolecular pumps (TMPs), turbomolecular pumps + cryo-surfaces, or cryopumps. Diffusion pumps were extensively used in the past and remain fairly widespread in laboratory applications. However, for industrial purposes their use appears to be restricted to systems requiring very high pumping speeds (S_0= thousands of L s^{-1}), particularly where substantial amounts of particulates are handled.

High-vacuum gas-transfer pumps (diffusion pumps, TMPs) must be combined with suitable backing pumps to work satisfactorily, and due consideration must be given to the sizing and specification of the latter. Typical pumping speed vs pressure curves for high-vacuum and backing pumps are shown in Figure 3.8.

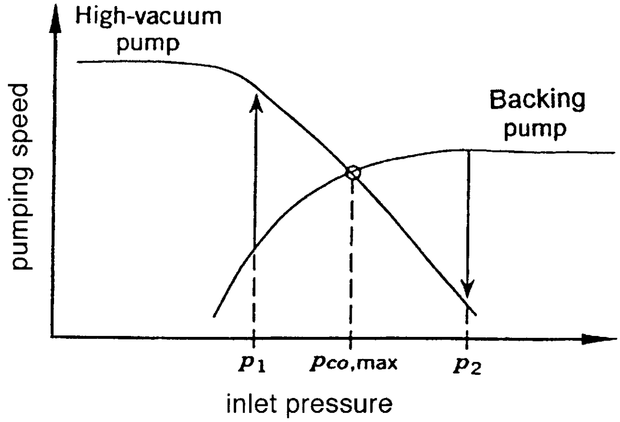


Figure 3.8 *Backing-pressure requirements in the changeover from roughing- (backing) to high-vacuum pumps*
(Reproduced from W. Schwarz, in ref. (f), p. 507; reprinted by permission of John Wiley & Sons Inc.)

In Figure 3.8, on the curve marked 'High-vacuum pump', it can be seen that the region of constant pumping speed (S_{max}) with inlet pressure leads to a region with declining pumping speed as the inlet pressure increases.

Further, on the curve marked 'Backing pump', at low enough inlet pressures, the pumping speed is low but increases to a constant level with increasing inlet pressure.

In the operation of high vacuum systems, initial pump-down involves the evacuation of the system from atmospheric pressure using a suitable roughing pump. Often, this is the same pump as that used to back the high-vacuum pump. A critical activity in the pump-down sequence involves switching from the backing (forevacuum) pump to the high-vacuum pump. It is inevitable that this switch-over will take place in the pressure range where the pumping speed of the high vacuum pump is declining. To minimise the effect of switch-over on the vacuum system, a pressure should be chosen (i) where the S_{eff} of the high vacuum pump is $\geq S_{eff}$ of the backing pump ($p_{co,max}$ in Figure 3.8) and (ii) the backing pump must be able to maintain a low enough backing pressure to maintain satisfactorily the operation of the high vacuum pump. In Figure 3.8, the switch-over pressure (p_2) is greater than $p_{co,max}$. This would cause the backing pressure to rise because $S_{eff,HV}$ is so low, possibly causing a change back to the backing pump. The cycle may be repeated several times. If a switch-over pressure (p_1) is selected then, although the roughing time may be extended, $S_{eff,HV}$ will be higher, bringing about a more rapid fall in chamber pressure.

3.3.1 Diffusion Pumps

Operation. In a diffusion pump, the pump fluid is heated so that a vapour pressure of 1–10 mbar is established in the boiler. The vapour rises in the jet assembly where it is expanded through nozzles and enters the space between the nozzle and the cooled wall of the pump at high supersonic velocity. Pumping action is based on the transfer of momentum in collisions between the high speed (several times the speed of sound) pump fluid vapour molecules and particles that have entered the vapour jet.

A possible problem with diffusion pumps is that of backstreaming whereby pump fluid molecules emerge, particularly from the top jet, in the direction of the chamber, where they can condense. Oil contamination can be significantly reduced by the use of baffles (cold-cap, shell) and traps between the pump and the system.

Pumping speed. The pumping speed of a diffusion pump as a function of the inlet pressure follows the shape of the general curve in Figure 3.9.

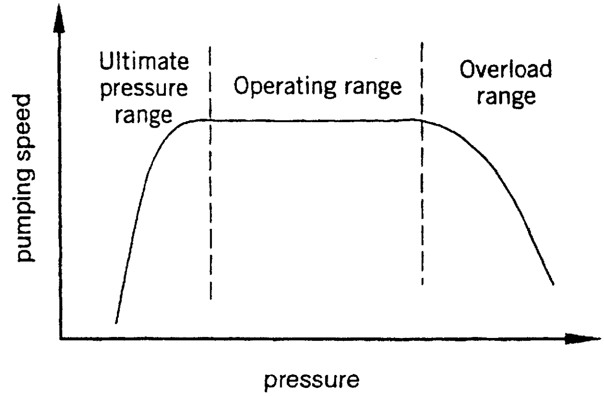


Figure 3.9 *General variation with pressure of the pumping speed of a high vacuum pump* (Reproduced from W. Schwarz, in ref. (f), p. 525; reprinted by permission of John Wiley & Sons Inc.)

In the operating range, the pumping speed of a diffusion pump is relatively high and constant. The decline in the pumping speed in the high vacuum region as the ultimate pressure is approached is given by:

$$S = S_{\text{max}}\left(1 - \frac{p_{\text{ult}}}{p}\right) \tag{3.14}$$

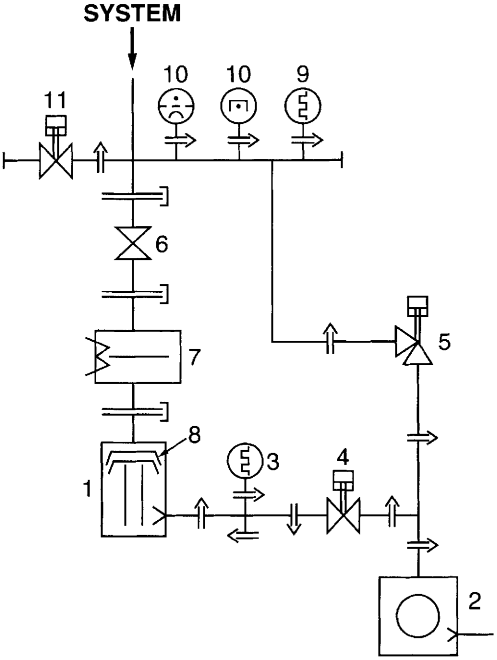
where S_{max} = the maximum pumping speed (the plateau)
p_{ult} = the ultimate pressure of the pump (at sufficiently low backing pressures, this is determined mainly by the vapour pressure of the pump fluid at the temperature of the walls, baffles and traps near the pump inlet)
p = system pressure.

At the high pressure end of the S vs p_{inlet} curve, (here labelled, overload region; also known as the forepressure break-down region), S declines from S_{max} until a critical pressure is reached in the backing line (critical backing pressure or forevacuum tolerance) which, if exceeded, causes the pumping action of the diffusion pump to cease.

Example 3.10

The diagram below shows a manually operated, diffusion-pumped high vacuum pump set.

(a) Identify the components numbered in the diagram and describe their function where necessary.
(b) Describe the sequence of operations to pump down the system if the latter is vented to atmosphere but pumps 1 and 2 are working and connected by valve 4.



(a) 1 = Diffusion pump
2 = Forevacuum pump (here, a two-stage, oil-sealed rotary vane pump); also used as a roughing pump
3 = Pirani gauge to monitor the backing line pressure
4 = Backing line valve
5 = Roughing line valve
6 = High vacuum valve
7 = Cooled shell baffle
8 = Cold-cap baffle
9 = Pirani gauge on system to indicate the pressure to open valve 6
10 = High vacuum gauge on system
11 = Venting valve

(b)
- Valve 11 is closed.
- After closing valve 4, valve 5 is opened and the system is roughed out. (During this operation, it is necessary to monitor the backing line pressure (gauge 3) to ensure that it remains below the critical backing pressure.)
- The system pressure is also monitored (gauge 9). When it reaches an appropriate level (see Figure 3.8 and associated comments), valve 5 is closed and valve 4 is opened and the high vacuum valve (valve 6) is opened.
- The monitoring of gauge 3 is continued.
- When gauge 9 indicates a sufficiently low pressure (usually (1 to 5) × 10^{-3} mbar), gauge 10 can be operated.

Note: It is usual to have a combined gauge accepting signals from the gauge heads 9 and 10 and automatically switching from 9 to 10 and *vice versa*.

Example 3.11

A diffusion pump has a pumping speed of $1000\,\mathrm{L\,s^{-1}}$ at $p_{\mathrm{in}} \leq 10^{-3}$ mbar, falling to $400\,\mathrm{L\,s^{-1}}$ at 10^{-2} mbar. The critical backing pressure for the pump is 4×10^{-1} mbar.

(a) Calculate the minimum size of the backing pump if the diffusion pump is brought in at 10^{-2} mbar.
(b) If the diffusion pump was brought in at 10^{-3} mbar, what would be the minimum size of the backing pump?

(a) At 10^{-2} mbar, the throughput of the diffusion pump is:

$$\begin{aligned} q_{\max} &= p_{\mathrm{in}} \times S_{\mathrm{eff,DP}} \\ &= 10^{-2}\,\mathrm{mbar} \times 400\,\mathrm{L\,s^{-1}} \\ &= 4\,\mathrm{mbar\,L\,s^{-1}} \end{aligned}$$

From the continuity equation:

$$q_{\max} = S_{\text{eff,back}} \times p_{\text{crit}}$$

Based on the above an *approximate* value of $S_{\text{eff,back}}$ can be found:

$$\begin{aligned} S_{\text{eff, back}} &= \frac{q_{\max}}{p_{\text{crit}}} \\ &= \frac{4\,\text{mbar L s}^{-1}}{0.4\,\text{mbar}} \\ &= \underline{10\,\text{L s}^{-1}\ (\sim 36\,\text{m}^3\,\text{h}^{-1})} \end{aligned}$$

Since the pumping speed of the backing pump may be declining, a series of curves has been calculated for possible backing pumps ($200\,\text{m}^3\,\text{h}^{-1}$, $100\,\text{m}^3\,\text{h}^{-1}$, $50\,\text{m}^3\,\text{h}^{-1}$ and $25\,\text{m}^3\,\text{h}^{-1}$) showing the variation of throughput q with backing pump inlet pressure (Figure 3.10). Marked on the curves are p_{crit} for the diffusion pump and $q_{\max}$.

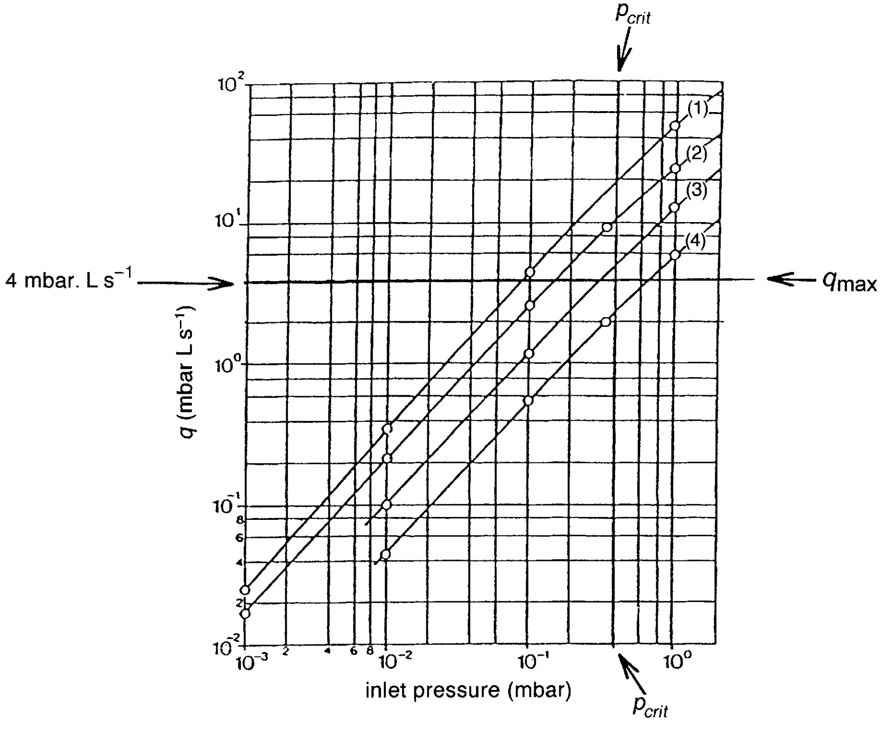


Figure 3.10 *Variation in throughput with inlet pressure for backing pumps with a range of pumping speeds:* (1), *$200\,m^3\,h^{-1}$*; (2), *$100\,m^3\,h^{-1}$*; (3), *$50\,m^3\,h^{-1}$*; (4), *$25\,m^3\,h^{-1}$*

From this, it can be seen that pump (4) cannot handle the gas load without the pressure rising above p_{crit}. Pump (3) can deal with the gas load but the pressure established is too close to p_{crit} (take into account some performance decline of the backing pump). Realistically, only pumps (1) or (2) would suffice.

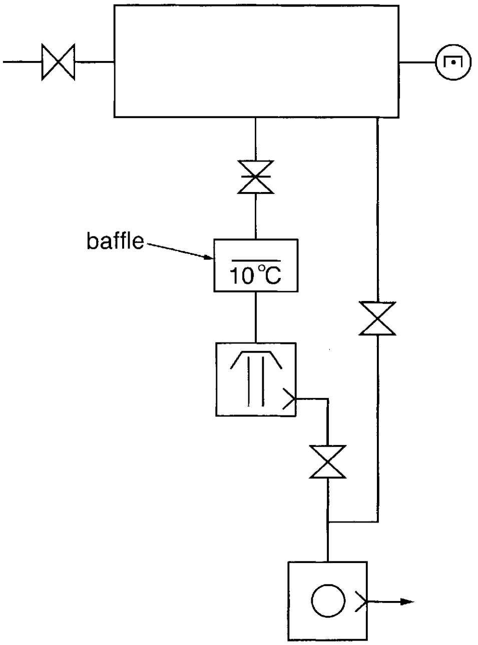
(b) If the diffusion pump was only operated at $p_{\text{in}} \leq 10^{-3}$ mbar:

$$\begin{aligned} q_{\max} &= 10^{3}\,\mathrm{L\,s^{-1}} \times 10^{-3}\,\mathrm{mbar} \\ &= 1\,\mathrm{mbar\,L\,s^{-1}} \end{aligned}$$

In this case, all four pumps would maintain $p_{\text{back}} < p_{\text{crit}}$ (2×10^{-1} mbar for pump (4)) but pumps (3) and (2) (50 m^3 h^{-1} and 100 m^3 h^{-1}) would easily be sufficient.

Example 3.12

The diagram below shows a conventional diffusion-pumped system.



For this system, the following are known:

- pumping speed of the diffusion pump for air at pressures below 10^{-4} mbar = 3000 L s^{-1}
- conductance of the baffle above the DP = 3000 L s^{-1}

- conductance of the high vacuum valve (DN 250 ISO-K, right-angle) = 2700 L s^{-1}

What is the effective pumping speed of the diffusion pump at the chamber?

$$\frac{1}{S_{\text{eff}}} = \frac{1}{S_0} + \frac{1}{C_{\text{tot}}}$$

$$\frac{1}{C_{\text{tot}}} = \frac{1}{C_{\text{baffle}}} + \frac{1}{C_{\text{HV valve}}}$$

$$\therefore \quad \frac{1}{C_{\text{tot}}} = \frac{1}{3000} + \frac{1}{2700}$$

$$C_{\text{tot}} = 1421 \text{ L s}^{-1}$$

$$\therefore \quad \frac{1}{S_{\text{eff}}} = \frac{1}{3000} + \frac{1}{1421}$$

$$S_{\text{eff}} = \underline{964 \text{ L s}^{-1}}$$

Example 3.13

The maximum permissible backing pressure (the critical backing pressure, p_{crit}) for a diffusion pump (pumping speed = $S_{\text{eff,DP}}$) is 2×10^{-1} mbar. If the pump is used only at inlet pressures (p_{in}) of 10^{-3} mbar or below, calculate the speed of the backing pump (S_{back}) in terms of $S_{\text{eff,DP}}$.

Also calculate the minimum pumping speed of the backing pump if a 500 L s^{-1} diffusion pump is to be used only at pressures (a) $\leq 10^{-3}$ mbar and (b) 10^{-4} mbar.

If Q is the throughput of the pump at the chamber, then:

$$Q = p_{\text{in}} \, S_{\text{eff,DP}}$$

This must be handled by the backing pump whilst maintaining $p_{\text{backing line}} \leq p_{\text{crit}}$.

$$\textit{i.e.} \quad p_{\text{in}} \, S_{\text{eff,DP}} = S_{\text{back}} \, p_{\text{crit}}$$

$$\therefore \quad S_{\text{back}} \geq \frac{p_{\text{in}} \, S_{\text{eff,DP}}}{p_{\text{crit}}}$$

(a) If $p_{\text{in}} = 10^{-3}$ mbar and $p_{\text{crit}} = 0.2$ mbar

$$\text{then } S_{\text{back}} \geq 5 \times 10^{-3}\, S_{\text{eff,DP}}$$

$$\begin{aligned} S_{\text{back}} &\geq 5 \times 10^{-3} \times 500\,\text{L s}^{-1} \\ &= 2.5\,\text{L s}^{-1} \\ &= 9\,\text{m}^3\,\text{h}^{-1} \end{aligned}$$

Usually, a two-stage pump with a pumping speed ~ 20% higher, *i.e.* about 11 $\text{m}^3\,\text{h}^{-1}$ would be chosen if the backing line had adequate conductance.

(b) At $p_{\text{in}} = 10^{-4}$ mbar, using the above formula, the backing pump should be a two-stage pump with speed = 1 $\text{m}^3\,\text{h}^{-1}$. However, if unexpected gas sources occur, the backing pump would be insufficient. Usually, however, a backing pump which is the next pumping speed up in the manufacturer's range is selected.

With diffusion-pumped systems such as that shown schematically in Example 3.12, there is a gas throughput from the backing port of the diffusion pump even with the high vacuum valve closed. Experience shows that this amounts to ~ 2 × 10^{-3} mbar L s^{-1} and is generally independent of the pumping speed of the diffusion pump. During extended periods of chamber roughing, when the backing line valve is closed, it is possible that the backing line pressure could approach p_{crit}. For this reason, a small 'holding' pump may have to be fitted to maintain $p_{\text{backing}} \leq p_{\text{crit}}$. Whether or not a holding pump is necessary can be determined and, if so, its size can be estimated.

Example 3.14

A diffusion pump (S_0 = 3000 L s^{-1}) has a maximum permissible for-evacuum pressure of 0.6 mbar. There is a length of tubing, 1 m × DN63 ISO-K, between the diffusion pump backing port and the backing valve. If the usual pressure in the backing line is 2 × 10^{-2} mbar, calculate the length of time the diffusion pump could be isolated from its backing pump with the inlet valve closed.

Volume of backing line between the DP outlet and the backing valve

$$= \pi \times (3.5\,\text{cm})^2 \times 100\,\text{cm} = 3850\,\text{cm}^3\ (3.85\,\text{L})$$

With

$$q_{\text{in}} = 2 \times 10^{-3}\,\text{mbar L s}^{-1}\text{, the allowable time} = \frac{\text{volume} \times \text{pressure rise}}{q_{\text{in}}\ (\text{from backing port})}$$

$$= \frac{3.85\,\text{L} \times (0.6 - 0.02)\,\text{mbar}}{2 \times 10^{-3}\,\text{mbar L s}^{-1}}$$

$$= \underline{1117\,\text{s}\ (18.6\,\text{min})}$$

Example 3.15

In Example 3.12, the diffusion pump is to be operated for 1 h with an inlet pressure of 10^{-5} mbar with the backing pump switched off (and the backing valve closed) to eliminate the effect of vibration from the backing pump on the system. Calculate the volume of the backing line to achieve this if the critical backing pressure of the DP is 0.6 mbar.

Gas flux emerging from backing port of DP ($q_{pV,\mathrm{total}}$) is given by:

$$q_{pV,\mathrm{tot}} = q_{pV,\mathrm{DP\ inlet}} + q_{pV,\mathrm{DP\ generated}}$$

$$\begin{aligned} \therefore \quad q_{pV,\mathrm{total}} &= p_{\mathrm{in}} S_{\mathrm{eff,DP}} + 2 \times 10^{-3}\,\mathrm{mbar\,L\,s^{-1}} \\ &= 1 \times 10^{-5}\,\mathrm{mbar} \times 964\,\mathrm{L\,s^{-1}} + 2 \times 10^{-3}\,\mathrm{mbar\,L\,s^{-1}} \\ &= 9.6 \times 10^{-3}\,\mathrm{mbar\,L\,s^{-1}} + 2 \times 10^{-3}\,\mathrm{mbar\,L\,s^{-1}} \\ &= 1.2 \times 10^{-2}\,\mathrm{mbar\,L\,s^{-1}} \end{aligned}$$

If the acceptable pressure rise in the backing line is approx. 0.6 mbar (actually, $p_{\mathrm{crit}} - p_{\mathrm{back,normal}}$), then:

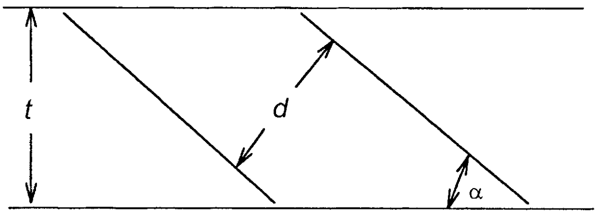
$$\begin{aligned} V &= \frac{q_{pV,\mathrm{tot}} \times \Delta t}{\Delta p} \\ &= \frac{1.2 \times 10^{-2}\,\mathrm{mbar\,L\,s^{-1}} \times 3600\,\mathrm{s}}{0.6\,\mathrm{mbar}} \\ &= \underline{72\,\mathrm{L}} \end{aligned}$$

Obviously, a separate backing volume must be incorporated into the backing line.

3.3.2 Turbomolecular Pumps

A turbomolecular pump is a multi-stage, bladed turbine in which the rotor is driven at high rotational speeds so that the peripheral speed of the blades is of the same order of magnitude as the thermal velocity ($\bar{c}$) of the gas particles to be pumped. The combination of a rotor and stator disc is one stage in a TMP. Pumped gas is compressed along the rotor-stator assembly and passed to a backing pump/pump-set for further compression to atmospheric pressure.

Turbomolecular pumps made up solely of bladed stages are often categorised as 'classic' turbomolecular pumps. Those with compound rotors, consisting of bladed- and drag stages, are often referred to as 'wide-range' or 'hybrid' TMPs.



α = blade angle d = blade distance t = blade thickness

Figure 3.11 *The parameters of turbomolecular pump blades*

Turbomolecular pumps are highly-regarded as 'clean' pumps. They can be regarded as having constant pumping speed when normal rotational speed has been achieved. Important characteristics of turbomolecular pumps are the compression ratio and pumping speed. The compression ratio for a particular gas (A) is given in Equation (3.15):

$$k_A = \frac{p_{A,\text{forevac}}}{p_{A,\text{inlet}}} \tag{3.15}$$

i.e. the ratio between the partial pressure of component A at the forevacuum flange and that at the inlet of the TMP. The maximum compression ($K_{\max}$, or k_0) is found at zero throughput.

The value of ($K_{\max}$, k_0) is also given by:

$$K_{\max} = ugx/\bar{c} \tag{3.16}$$

where $\bar{c}$ is the mean velocity of gas being pumped, g is a factor dependent on rotor–stator geometry, u is the rotor blade speed and x is the number of stages in the TMP.

As $\bar{c} \propto M^{-\frac{1}{2}}$, where M is the molar mass of the pumped gas, the dependence of $K_{\max}$ on M is marked, and typical values are given in Table 3.7.

Table 3.7 *Variation of* K_{max} *for various gases*

Gas	Range of $K_{\max}$ values[a]
H_2	10^2 to 10^5
He	10^3 to 10^7
N_2	5×10^6 to 10^{10}

[a] Value depends on manufacturer of pump.

The increase of $K_{\max}$with M means that heavy molecules have a low probability of backflowing through the TMP, hence the 'cleanliness' of turbomolecular pumps.

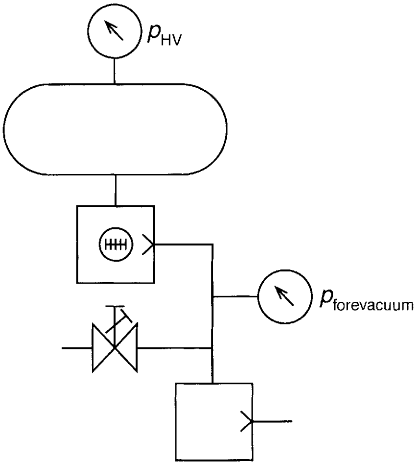
From Equation (3.16), $\log K_{\max} \propto \sqrt{M}$

For 'classic' turbomolecular pumps, $K_{\max}$ is also dependent on the forevacuum pressure, decreasing at values of $p_{\text{forevac}} \gtrsim 10^{-3}$ mbar (the pressure at which the mean free path of the gas becomes less than the blade distance (see Figure 3.11)).

Over a large range of inlet pressures, the pumping speed of a turbomolecular pump remains constant. When the intake pressure increases to the 10^{-2} to 10^{-3} mbar range, the pumping speed begins to decrease markedly, because of the transition from molecular flow to other flow regimes. Turbomolecular pumps can, however, maintain their rotational frequency at inlet pressures up to 1 mbar and therefore deal with relatively high intake pressures for reasonable periods of time (a few minutes). Although the pumping speed of turbomolecular pumps for lighter gases is lower than that for N_2 and air (owing to the lower pumping probability of the lighter gases), the inlet aperture will have an increased conductance for lighter gases. This gives rise to a pumping speed for H_2 and He which is reasonably close (0.8–0.9) to the speed for N_2.

Example 3.16

For the measurement of the compression ratio (k) of a turbomolecular pump, a test volume was attached to the pump inlet *via* a CF-flange.



The test volume was fitted with a suitable ionisation gauge and test gas was admitted to the system *via* a variable leak valve fitted to the backing line of the TMP. The system is shown in the diagram.

Measurement of the compression ratio was carried out after the system had been pumped down to its base pressure ($p_{\text{basc}} < 10^{-8}$ mbar). By opening the variable leak valve, the test gas (in this case H_2) was admitted to the backing line and after equilibrium had been established, p_{backing} and p_{HV} were measured.

(a) If $p_{\text{forevac}} = 5 \times 10^{-3}$ mbar and $p_{\text{HV}} = 1 \times 10^{-6}$ mbar, what is the value for k_{H_2}?
(b) The amount of H_2 admitted was increased so that $p_{\text{forevac}} = 6 \times 10^{-2}$ mbar and $p_{\text{HV}} = 3 \times 10^{-5}$ mbar. What is the new value for k_{H_2}?
(c) Why is there a difference between (a) and (b)?
(d) Why is k_{H_2} of interest on TMP-pumped systems?

(a) According to Equation (3.15):

$$k_{H_2} = \frac{p_{H_2,\text{forevac}}}{p_{H_2,\text{HV}}}$$

$$\therefore \quad k_{H_2} = \frac{5 \times 10^{-3}\ \text{mbar}}{1 \times 10^{-6}\ \text{mbar}}$$

$$= 5000$$

(b)

$$k_{H_2} = \frac{6 \times 10^{-2}\ \text{mbar}}{3 \times 10^{-5}\ \text{mbar}}$$

$$= 2000$$

(c) As p_{H_2} in the backing line increases, backflow in the TMP increases.
(d) In baked high and UHV systems, outgassing of H_2 (significant with air-melted metals) from the system occurs. k_{H_2} and p_{H_2} in the backing line will determine the lowest attainable pressure in the system.

Example 3.17

Using the same experimental set-up as described in Example 3.16 but with a different type of turbomolecular pump, $k_{N_2} = 8 \times 10^8$ was obtained with $p_{N_2,\text{forevac}} = 5 \times 10^{-2}$ mbar. If H_2 had been admitted instead of N_2 to the same forevacuum pressure, estimate $p_{H_2,\text{HV}}$.

According to Equation (3.16):

$$\log k_{\text{gas}} \propto \sqrt{M_{\text{gas}}}$$

$$\therefore \quad \frac{\log k_{N_2}}{\log k_{H_2}} = \frac{\sqrt{28}}{\sqrt{2}} = 3.74$$

$$\therefore \quad 3.74 \log k_{H_2} = \log k_{N_2} = 8.903$$

$$\therefore \quad \log k_{H_2} = 2.38$$

$$\therefore \quad k_{H_2} = 240$$

$$k_{H_2} = \frac{p_{H_2,\text{forevac}}}{p_{H_2,HV}}$$

$$p_{H_2,HV} = \frac{5 \times 10^{-2}\,\text{mbar}}{240} = \underline{2 \times 10^{-4}\,\text{mbar}}$$

Note: p_{HV} was measured with an ionisation gauge, the reading of which is gas-dependent. The estimate of $p_{H_2,HV}$ would not, therefore, be shown on the gauge and an appropriate correction factor must be applied (see Chapter 5).

Example 3.18

A UHV chamber for LEED studies is evacuated to ultra-high vacuum with a combination of pumps consisting of a turbomolecular pump (backed with an oil-sealed rotary vane pump) and a titanium sublimation pump (TSP). When the chamber is evacuated by both pumps, a total pressure of 4×10^{-9} mbar is achieved and residual gas analysis shows that this consists of 50% Ar + 50% H_2.

On reaching 4×10^{-9} mbar, the valve to the TSP is closed. The chamber pressure rises to 8×10^{-9} mbar.

(a) Calculate the new partial pressure of H_2 in the system.

(b) If the effective pumping speed of the turbomolecular pump is 100 L s^{-1} (independent of gas type), calculate the pumping speed of TSP for H_2. Calculate the pV-throughput of H_2 and Ar into the chamber.

(a) Noble gases will not be pumped by the TSP (see Section 3.4.2). Initially:

$$p_{\text{tot}} = 4 \times 10^{-9}\,\text{mbar consisting of } 50\%\ \text{Ar} + 50\%\ H_2$$
$$= p_{Ar} + p_{H_2}$$
$$= 2 \times 10^{-9}\,\text{mbar} + 2 \times 10^{-9}\,\text{mbar}$$

On isolation of the TSP, the pressure rises to 8×10^{-9} mbar,

$$\begin{aligned}\Delta p &= 8\times10^{-9}\,\text{mbar} - 4\times10^{-9}\,\text{mbar}\\ &= 4\times10^{-9}\,\text{mbar}\end{aligned}$$

As the TMP is not an efficient pump for H_2, the pressure rise is predominantly due to H_2.

$$\begin{aligned}\therefore\quad \text{new } p_{\mathrm{H_2}} &= 2\times10^{-9}\,\text{mbar} + 4\times10^{-9}\,\text{mbar}\\ &= \underline{6\times10^{-9}\,\text{mbar}}\end{aligned}$$

(b) Initially:

$$p_{\text{tot}} = 4\times10^{-9}\,\text{mbar} = p_{\text{Ar}} + p_{\mathrm{H_2}}$$

$$\therefore\quad 4\times10^{-9}\,\text{mbar} = \frac{q_{pV,\text{Ar}}}{S_{\text{eff,TMP}}} + \frac{q_{pV,\mathrm{H_2}}}{S_{\text{eff,TMP}+}S_{\text{eff,TSP}}}$$

For Ar:

$$p_{\text{Ar}} = \frac{q_{pV,\text{Ar}}}{100\,\text{L s}^{-1}}$$

$$\begin{aligned}\therefore\quad q_{pV,\text{Ar}} &= 2\times10^{-9}\,\text{mbar}\times100\,\text{L s}^{-1}\\ &= \underline{2\times10^{-7}\,\text{mbar L s}^{-1}}\end{aligned}$$

With the TSP closed off:

$$p_{\text{tot}} = \frac{q_{pV,\text{Ar}} + q_{pV,\mathrm{H_2}}}{100\,\text{L s}^{-1}}$$

$$\therefore\quad 8\times10^{-9}\,\text{mbar} = \frac{2\times10^{-7}\,\text{mbar L s}^{-1}}{100\,\text{L s}^{-1}} + \frac{q_{pV,\,\mathrm{H_2}}}{100\,L\,s^{-1}}$$

$$\therefore\quad 8\times10^{-7}\,\text{mbar L s}^{-1} = 2\times10^{-7}\,\text{mbar L s}^{-1} + q_{pV,\mathrm{H_2}}$$

$$\therefore\quad \underline{q_{pV,\mathrm{H_2}} = 6\times10^{-7}\,\text{mbar L s}^{-1}}$$

Initially,

$$\text{As } 4\times10^{-9}\,\text{mbar} = \frac{2\times10^{-7}\,\text{mbar L s}^{-1}}{100\,\text{L s}^{-1}} + \frac{6\times10^{-7}\,\text{mbar L s}^{-1}}{100\,\text{L s}^{-1} + S_{\text{eff,TSP}}}$$

$$2\times10^{-9}\,\text{mbar} = \frac{6\times10^{-7}\,\text{mbar L s}^{-1}}{100\,\text{L s}^{-1} + S_{\text{eff,TSP}}}$$

$$S_{\text{eff,TSP}} = 200\,\text{L s}^{-1}$$

Example 3.19

Investigations were carried out on a small turbomolecular pump intended for use in a helium leak detector (see Chapter 4). Measurements at 24 °C of $K_{\text{max.He}}$ for a suitably backed nine-stage pump with a blade circumferential speed of 200 m s^{-1} yielded a value of 254.

(a) Calculate the compression ratio for N_2.

(b) If the maximum volume flow rate for the pump can be expressed as:

$$S = A(\bar{c}/4)[1 - \exp(-u/\bar{c})][1 - \exp(-gu/\bar{c})]$$

where A = area of the inlet flange (r = 24 mm) and g is the geometric factor, calculate $S_{N_2\text{eff}}$, at 24 °C if the conductance between the connection flange to the measurement chamber and the plane of the inlet rotor is 160 L s^{-1} for N_2 (set-up as figure in Example 3.16).

(a) From Equation (3.16):

$$K_{\max} = \exp(gzu/\bar{c})$$

Here $z = 9, u = 200 \text{ m s}^{-1}$

From $K_{\max}$, g can be calculated if $\bar{c}$ is known:

$$\bar{c} = 145.5\sqrt{(T/M)}$$

$$\therefore\ \bar{c}_{\text{He,297K}} = 1253.8 \text{ m s}^{-1}$$

$$\therefore\quad g = \ln K_{\text{max,He,297K}} \times (\bar{c}/zu)$$

$$= 5.54 \times \frac{1258.8 \text{ m s}^{-1}}{9 \times 200 \text{ m s}^{-1}}$$

$$\therefore\quad g = 3.86$$

Substituting this value for g in Equation (3.16),

$$K_{\text{max},N_2,297K} = \exp\left(\frac{3.86 \times 9 \times 200 \text{ m s}^{-1}}{473.9 \text{ m s}^{-1}}\right)$$

$$= \exp(14.66)$$

$$\therefore\quad \underline{K_{\text{max},N_2,297K} = 2.3 \times 10^6}$$

(b) $$S_0 = A(\bar{c}/4)[1 - \exp(-u/\bar{c})][1 - \exp(-gu/\bar{c})]$$

where $A = 18 \text{ cm}^2$, $\bar{c} = 473.9 \text{ m s}^{-1}$

Substituting the appropriate values

$$S_0 = \frac{18\ \text{cm}^2}{10^4} \times 118.5\ \text{m s}^{-1}[1 - \exp(-200/473.9)][1 - \exp(3.86 \times 200/473.9)]$$

$$= 18 \times 10^{-4}\ \text{m}^2 \times 118.5\ \text{m s}^{-1}[0.34][0.80]$$

$$= 0.058\ \text{m}^3\ \text{s}^{-1}$$

$$= 58\ \text{L s}^{-1}$$

If $C_{\text{connection}} = 160\ \text{L s}^{-1}$, $S_{\text{TMP,chamber}}$ is calculated from:

$$\frac{1}{S_{\text{TMP,ch}}} = \frac{1}{58\ \text{L s}^{-1}} + \frac{1}{160\ \text{L s}^{-1}}$$

$$\therefore \quad \underline{S_{\text{TMP,ch}} = 42.5\ \text{L s}^{-1}}$$

3.3.3 Cryopumps

Cryopumps produce very clean (see Section 3.1) vacua. They have high specific pumping speeds and can easily attain HV/UHV pressures. Cryopumping involves the removal of gas particles by means of surfaces cooled to 80 K or below. At sufficiently low temperatures, all gases, with the exception of He, condense to form a solid phase although the resulting pressure depends on the temperature of the condensate. A temperature of 20 K will achieve UHV levels for gases except Ne, He and H_2 (D_2). A phenomenon that enables the removal of the latter group of gases is cryosorption whereby the adsorption of the difficult-to-pump gases on a porous solid (such as activated charcoal) at 20 K or below readily occurs. For example, activated charcoal at 20 K will give an equilibrium pressure with H_2 of about 5×10^{-7} mbar; at 10 K, a pressure of $\sim 10^{-14}$ mbar is established.

To achieve temperatures low enough for effective gas removal, two methods are generally used. One involves the use of a cryogen, *e.g.* liquid N_2, liquid He *etc.* The other method uses a cryocooler in which a suitable gas (usually high purity He) is involved in an expansion–compression cycle. Commercially exploited cycles include the Gifford–McMahon cycle (see ref. (g), p. 114). Cryogen-based pumps range from simple LN_2-cooled traps to large continuous-flow cryopumps using liquid-He-cooled surfaces to remove gases and having pumping speeds for N_2 in the range 10^5 to $10^7\ \text{L s}^{-1}$. Gifford–McMahon-type refrigerators, although having relatively low cooling power (typically, for a two-stage cooler, the first stage operates at temperatures between 30 and 80 K with a power of

10–100 W; the second stage operates at temperatures between 8 and 20K with cooling powers in the range 2 to 10 W) are more convenient to use in routine applications for pumping speeds up to ~ 10^4 L s^{-1}.

3.3.3.1 Heat Loads in Cryogenic Systems. In any cryogenic system, the heat load transferred to the cold surface determines the refrigeration capacity required to maintain the low temperature. Analysis has shown that the thermal loads received by a surface at cryogenic temperatures are due to:

1 *Thermal radiation* ($\dot{Q}_{\text{rad}}$)
An unshielded cryosurface (area A_c, temperature T_c, emissivity ε_c) receives from the surrounding vessel wall (corresponding values A_w, T_w, ε_w).

$$\dot{Q}_{\text{rad}} = f A_c \sigma (T_w^4 - T_c^4) \tag{3.17}$$

where σ = Stefan–Boltzmann constant
$= 5.671 \times 10^{-8}\ \mathrm{W\,m^{-2}\,K^{-4}}$

and f = a radiation emissivity factor $= \dfrac{1}{\dfrac{1}{\varepsilon_c} + \dfrac{A_c}{A_w}\left(\dfrac{1}{\varepsilon_w} - 1\right)}$ if A_w encloses A_c.

With cryosurfaces, it is convenient to reduce ε as much as possible by polishing or gold-plating (ε ~ 0.03). The accumulation of condensate changes ε considerably, however, and, for condensate films a few millimetres thick, it can increase significantly and approach 0.9 (ε for a black body = 1).

2 *Heat load due to gas condensation* ($\dot{Q}_{\text{cond}}$)
This involves the heat that must be extracted from the gas to cool it to the trapping temperature and the enthalpy of condensation (or heat of adsorption) that must also be removed. This quantity increases with gas throughput.

3 *Heat load due to the thermal conductivity of the gas* ($\dot{Q}_{\text{th.c}}$)
There are gas particles between the cryosurface (T_c) and the warm surroundings. This quantity is negligible at low pressures but must be taken into account above 10^{-3} mbar.

$$\dot{Q}_{\text{tot}} = \dot{Q}_{\text{rad}} + \dot{Q}_{\text{cond}} + \dot{Q}_{\text{th.c}} \tag{3.18}$$

Of the terms in Equation (3.18), $\dot{Q}_{\text{rad}}$ predominates. It is extremely high when the cryopanel is surrounded by surfaces at normal ambient temperatures but can be reduced significantly by surrounding it with a shield at, say, approximately 80 K.

Example 3.20

The enthalpy difference between liquid He (LHe) and its vapour at 4.2 K is 20.9 kJ kg^{-1}. In a LHe cooled cryostat, 5 L He per hour are evaporated at 4.2 K. What is the cooling capacity of the cryostat (the density ρ of He at 4.2 K is 124.8 kg m^{-3})?

The evaporation of 1 kg LHe requires 20.9 kJ.

$$\begin{aligned}\rho_{\mathrm{He,4.2K}} &= 124.8\ \mathrm{kg\,m^{-3}}\\ &= 0.1248\ \mathrm{kg\,L^{-1}}\end{aligned}$$

Enthalpy difference between LHe and He vapour at 4.2 K

$$\begin{aligned}&= 20.9\ \mathrm{kJ\,kg^{-1}} \times 0.1248\ \mathrm{kg\,L^{-1}}\\ &= 2.61\ \mathrm{kJ\,L^{-1}}\end{aligned}$$

∴ Evaporation of 5 L/h of LHe

$$\begin{aligned}&= 2.61 \times 5\ \mathrm{kJ\,h^{-1}}\\ &= 13042\ \mathrm{J\,h^{-1}}\\ &= 3.6\ \mathrm{J\,s^{-1}}\\ &= \underline{3.6\ \mathrm{W\ at\ 4.2\ K}}\end{aligned}$$

Example 3.21

The transfer of heat to liquid cryogens gives rise to loss of cryogen. Calculate the result, in terms of volume of liquid cryogen lost, of the dissipation of 1 W into: (a) LHe at 4.2K, (b) LN$_2$ at 77.4 K. The enthalpy difference between LN$_2$ and its vapour at 77.4 K is 160.9 KJ L^{-1}.

(a) From Example 3.20, the enthalpy difference between LHe and He vapour at 4.2 K is 2610 J L^{-1}. The dissipation of 1W (1 J s^{-1}) would give rise to the loss of 1 L of LHe in 2610 s.

$$\text{This is equivalent to } \frac{3600}{2610}\ \text{L LHe per hour}$$

$$\underline{= 1.379\ \mathrm{L\,h^{-1}}}$$

(b) The enthalpy difference between LN$_2$ and its vapour at 77.4 K is equivalent to 160.9×10^3 J L^{-1} or 160.9 J cm^{-3}.

The dissipation of 1 W is therefore equivalent to the loss of 1 cm^3 in 160.9 s or:

$$\frac{3600}{160.9}\,\text{cm}^3\,\text{h}^{-1}$$
$$\underline{= 22.4\,\text{cm}^3\,\text{h}^{-1}}$$

Example 3.22

A major problem in the design of cryopumps is that of reducing the thermal load falling on the cryosurface.

(a) A flat cryosurface (A_c) at 20 K is faced by a parallel wall at 300 K. Calculate the radiant flux if $\varepsilon_c = 0.5$.
(b) In practice, A_c would be shielded by a baffle (A_b) at about 80 K. Calculate the radiant flux when $A_b = A_c$ and $\varepsilon_b = 0.1$.

(a) From Equation (3.17):

$$\dot{Q}_{\text{rad}} = f\,A_c\sigma(T_w^4 - T_c^4)$$

$$\text{where}\quad f = \frac{1}{\dfrac{1}{\varepsilon_c} + \dfrac{A_c}{A_w}\left(\dfrac{1}{\varepsilon_w} - 1\right)}$$

If $A_w \gg A_c$ then Equation (3.17) can be written for this example as:

$$\begin{aligned}\dot{Q}_{\text{rad}} &= \varepsilon_c\,A_c\sigma(300^4 - 20^4)\,\text{W}\\ &= 0.5A_c\,\text{m}^2 \times 5.671 \times 10^{-8}\,\text{W}\,\text{m}^{-2}\,\text{K}^{-4} \times (300^4 - 20^4)\,\text{K}^4\\ &= 0.5A_c\,\text{m}^2 \times 5.671 \times 10^{-8}\,\text{W}\,\text{m}^{-2}\,\text{K}^{-4} \times 8.099 \times 10^9\,\text{K}^4\\ &\underline{\cong 230\,\text{W}\,\text{m}^{-2}}\ \text{(very high for practical use)}\end{aligned}$$

Note: If $A_c = A_w$, $T_w = 300$ K and $\varepsilon_w = 0.5$:

$$\dot{Q}_{\text{rad}} = f\,A_c\sigma(300^4 - 20^4)\,\text{W}$$

$$\text{and}\quad f = \frac{1}{\dfrac{1}{0.5} + \left(\dfrac{1}{0.5} - 1\right)}$$

$$= 0.33$$

$$\begin{aligned}\therefore\quad \dot{Q}_{\text{rad}} &= 0.33\,A_c\sigma(300^4 - 20^4)\,\text{W}\\ &\underline{\cong 152\,\text{W}\,\text{m}^{-2}}\end{aligned}$$

(b) From Equation (3.17):

$$\dot{Q}_{\mathrm{rad}} = f A_{\mathrm{c}} \sigma (T_{\mathrm{b}}^4 - T_{\mathrm{c}}^4)$$

$$\text{where}\quad f = \frac{1}{\dfrac{1}{\varepsilon_{\mathrm{c}}} + \dfrac{A_{\mathrm{c}}}{A_{\mathrm{b}}}\left(\dfrac{1}{\varepsilon_{\mathrm{b}}} - 1\right)}$$

$$f = \frac{1}{\dfrac{1}{0.5} + \left(\dfrac{1}{0.1} - 1\right)}$$

$$= 0.09$$

$$\begin{aligned}\dot{Q}_{\mathrm{rad}} &= 0.09 A_{\mathrm{c}} \times 5.671 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}} \times (80^4 - 20^4)\,\mathrm{K^4} \\ &= 0.09 A_{\mathrm{c}} \times 5.671 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}} \times 4.08 \times 10^7\,\mathrm{K^4} \\ &= 0.09 A_{\mathrm{c}} \times 2.3\,\mathrm{W\,m^{-2}} \\ &= \underline{0.21\,\mathrm{W\,m^{-2}}}\ (\sim 0.1\%\ \text{of the unbaffled value})\end{aligned}$$

Example 3.23

An experimental liquid helium condensation cryopump has been constructed as a model for a large-scale pumping system to be used for handling high H_2/D_2 gas loads.

In the model pump, a LHe cryopanel (90 cm × 90 cm) made of silver-plated stainless steel is shielded at the rear by a parallel LN_2-cooled wall, polished on the panel side and, facing the vacuum system, by a LN_2-cooled chevron baffle (with a gas transmission of 20%). The He cryopanel is supplied from a stainless steel LHe reservoir ($A = 1.75\,\mathrm{m^2}$), wrapped in Al foil and protected by a LN_2 radiation shield of equal area.

(a) From the information given, calculate the approximate pumping speed for (i) H_2 (ii) N_2.
(b) Estimate the thermal loading on the LHe surfaces (panel, reservoir) in the absence of gas loads.

(a) Area of cryopanel at 4.2 K = 90 cm × 90 cm = 8100 cm^2 (0.81 m^2),

(i) From Equation (1.13):

$$S_{\mathrm{H_2}} = \frac{\bar{c}_{\mathrm{H_2}}}{4}\ \mathrm{m^3\,s^{-1}\,m^{-2}}$$

For H_2 at 293 K, using Equation (1.15):

$$\frac{\bar{c}_{H_2}}{4} = 36.38\sqrt{\frac{293}{2}}\,\mathrm{m\,s^{-1}}$$

$$= 440.27\,\mathrm{m\,s^{-1}}$$

$$\therefore\ S_{H_2} = 44\,\mathrm{L\,s^{-1}\,cm^{-2}}$$

For an unbaffled cryopanel, $A_c = 8100\,\mathrm{cm}^2$:

$$S_{H_2} = 3.57 \times 10^5\,\mathrm{L\,s^{-1}}$$

For a baffled panel (20% transmission):

$$S_{H_2,\mathrm{eff}} \cong 71000\,\mathrm{L\,s^{-1}}$$

(ii) The area-related pumping speed for N_2 on the 4.2 K panel can be similarly calculated.
For N_2 at 293 K:

$$\frac{\bar{c}_{N_2}}{4} = 117.68\,\mathrm{ms^{-1}}$$

$$\therefore\quad S_{N_2} = 11.8\,\mathrm{L\,s^{-1}\,cm^{-2}}$$

For the baffled 4.2 K panel (20% transmission):

$$\underline{S_{N_2,\mathrm{eff}} \cong 19000\,\mathrm{L\,s^{-1}}}$$

(b) Thermal loading on LHe surfaces
Panel

$$\dot{Q}_{\mathrm{rad}} = f\,A_c\sigma(77^4 - (4.2)^4)\,\mathrm{W}$$

$$f = \frac{1}{\dfrac{1}{\varepsilon_c} + \dfrac{A_c}{A_b}\left(\dfrac{1}{\varepsilon_b} - 1\right)}$$

For the silvered cryopanel (4.2 K) and the radiation-shield walls facing the 4.2 K surface, let $\varepsilon = 0.1$. Let A_c and A_b be the areas of the 4.2 K panel and the radiation shield, respectively. Let $A_b \cong 2A_c$.

$$\therefore\quad f = \frac{1}{\dfrac{1}{0.1} + \dfrac{1}{2}\left(\dfrac{1}{0.1} - 1\right)} = \frac{1}{14.5} = 0.069$$

$$\therefore \quad \dot{Q}_{\text{rad}} = 0.069 \times 0.81\,\text{m}^2 \times 5.671 \times 10^{-8}\,\text{W m}^{-2}\,\text{K}^{-4} \times (77^4 - (4.2)^4)\,\text{K}^4$$
$$= 0.1\,\text{W}$$

Reservoir

$$\dot{Q}_{\text{rad}} = f A_{\text{res}} \sigma (T_{\text{sh}}^4 - T_{\text{res}}^4)$$

where subscripts 'sh' and 'res' apply to the radiation shield and the reservoir, respectively.

$$\dot{Q}_{\text{rad}} = f \times 1.75\,\text{m}^2 \times 5.671 \times 10^{-8}\,\text{W m}^{-2}\,\text{K}^{-4} \times (77^4 - (4.2)^4)\,\text{K}^4$$

$$f = \frac{1}{\dfrac{1}{\varepsilon_{\text{res}}} + \dfrac{A_{\text{res}}}{A_{\text{sh}}}\left(\dfrac{1}{\varepsilon_{\text{sh}}} - 1\right)}$$

If $\varepsilon_{\text{res}} = \varepsilon_{\text{sh}} = 0.1$ and $A_{\text{res}} = A_{\text{sh}}$

$$f = 0.053$$

$$\therefore \quad \dot{Q}_{\text{rad}} = 0.053 \times 1.75\,\text{m}^2 \times 5.671 \times 10^{-8}\,\text{W m}^{-2}\,\text{K}^{-4} \times (77^4 - (4.2)^4)\,\text{K}^4$$
$$= 0.185\,\text{W}$$

$\therefore$ Total thermal loading (without gas load) on the LHe-cooled surfaces

$$= \dot{Q}_{\text{rad,panel}} + \dot{Q}_{\text{rad,res}}$$
$$= 0.29\,\text{W}$$

(This would give rise to a He loss of 400 $\text{cm}^3\,\text{h}^{-1}$.)

3.3.3.2 Characteristics of Cryopumps. Important characteristics are:

(i) pumping speed
(ii) ultimate pressure
(iii) starting pressure
(iv) crossover pressure
(v) up-time (before regeneration is required)

Pumping speed. So far, the maximum area-related pumping speed (collision rate, S_A) has been used in calculations. For a cryopanel built into a chamber with $A_{\text{cryo}} < A_{\text{chamber}}$, the pumping speed is given by:

$$S = A_c S_A \alpha \left(1 - \frac{p_{\text{ult}}}{p}\right) \tag{3.19}$$

where A_c = area of the cryopanel
S_A = the maximum area-related pumping speed
α = the probability of condensation (at sufficiently low temperatures, $\alpha = 1$ for all gases)
p_{ult} = ultimate pressure (see below)
p = pressure in the chamber

Ultimate pressure. This refers to the lowest pressure that can be reached in a system with negligible gas sources. For cryocondensation, a situation is reached where the condensation flux density is equal to the evaporation flux density. If $A_c \ll A_{vessel\,wall}$, this corresponds to the ultimate pressure giving:

$$p_{ult} = p_s \sqrt{\frac{T_w}{T_c}} \tag{3.20}$$

where p_s = vapour pressure of the condensate at T_c (see Table 3.8)
T_c = temperature of the cryopanel
T_w = temperature of the vessel (= T_{gas})

Table 3.8 *Vapour pressures (in mbar) at temperature* T*(K) for a range of gases*

	T(K) required for p_s(mbar)						
Gas	10^{-10}	10^{-8}	10^{-6}	10^{-4}	10^{-2}	10^{0}	10^{1}
H_2	2.98	3.47	4.17	5.22	6.78	9.3	11.4
N_2	21.0	23.5	26.8	31.1	37.0	46.3	53.0
Ar	23.5	26.6	30.3	35.4	42.7	53.5	61.3
CH_4	28.0	31.7	36.5	43.0	52.2	66.1	76.1
Xe	44.8	50.4	57.7	67.4	81.0	101.8	116.2
CO_2	68.0	75.6	85.0	97.2	113.3	135.8	151.3
H_2O	129.2	143.5	160.8	183.4	212.8	252.9	280.2

(Reproduced from R.A. Haefer, *Kryovakuumtechnik*, Springer-Verlag, Berlin, 1981, pp. 126–127)

Starting pressure. In principle, a cryopump could be started at atmospheric pressure. However, a thick layer of condensate of gases, easily removed by pre-evacuation, would be formed, restricting the capacity of the cryopump in its working phase. Further, at $p > 10^{-3}$ mbar, the thermal conductivity of the gas would present a high heat load to the cryosurface.

Crossover pressure. If a refrigerator cryopump is attached to a vacuum system *via* a valve and the pump is already cold, the crossover pressure represents the maximum pressure of gas at 293 K on the system side which, when admitted to the pump, does not increase the temperature of the cryopanel above 20 K.

An empirical relationship (see ref. (e), p. 57) gives:

$$p_{\text{crossover}} \leq \frac{35}{V}\dot{Q}_2 \,\text{mbar} \qquad (3.21)$$

where V is the system volume (in L) and $\dot{Q}_2$ is the second stage refrigerating power at 20 K (in W).[3]

Example 3.24

In a chamber, a source of Xe ions produces a mass flow of 1.0 mg s^{-1}. The pressure in the chamber must be maintained at 5×10^{-6} mbar at 293 K using cryopumping. Assess the specifications of such a system.

From Equations (2.1 and 2.4):

$$q_{pV} = \dot{m}\frac{RT}{M}$$

$$\therefore \quad q_{pV,\text{Xe}} = \frac{1 \times 10^{-3}\,\text{g s}^{-1} \times 83.14\,\text{mbar L gmol}^{-1}\,\text{K}^{-1} \times 293\,\text{K}}{131.1\,\text{g gmol}^{-1}}$$

$$= 0.186\,\text{mbar L s}^{-1}$$

To maintain 5×10^{-6} mbar in the presence of this throughput, the minimum pumping speed required is (from Equation (2.7)):

$$S_{\text{eff}} = \frac{q_{pV,\text{Xe}}}{p}$$

$$= \frac{0.186\,\text{mbar L s}^{-1}}{5 \times 10^{-6}\,\text{mbar}}$$

$$= 37\,200\,\text{L s}^{-1}\ (\text{say } 40\,000\,\text{L s}^{-1})$$

The temperature interval corresponding to a vapour pressure for Xe in the range 10^{-6} to 10^{-8} mbar is 58–51 K (see Table 3.8). Taking into account the temperature gradient normally associated with thick (few mm) condensate layers, we conclude that a temperature of 50 K or lower must be established on the pumping surface.

The area-related pumping speed achieved by a cryopanel can be calculated from Equation (3.19):

$$S = A_c S_A \alpha \left(1 - \frac{p_s}{p}\sqrt{\frac{T_w}{T_c}}\right)$$

If it is assumed that $\alpha = 1$, $T_w = 293$ K, $T_c = 50$ K and that $p \gg p_s$, then $S = A_c S_A$ and from Equation (1.15):

$$S_A = 36.38\sqrt{\frac{293}{131.1}}\,\mathrm{m^3\,s^{-1}\,m^{-2}}$$

$$\underline{= 5.44\ \mathrm{L\,s^{-1}\,cm^{-2}}}$$

For a pumping speed of 40 000 L s^{-1}, the minimum required cryopanel area for an unshielded pump would be $A_c = S_{eff} / S_A \cong 7400\ \mathrm{cm}^2$. This value is certainly a lower limit since it ignores desorption from the vessel walls, small leaks, *etc.* It would be better to have $A_c = 9000\ \mathrm{cm}^2$ which is about 20% higher.

For an unshielded pump with thermal radiation from the walls at 293 K falling on the cold surface, Equation (3.17) states:

$$\dot{Q}_{rad} = f A_c \sigma (T_w^4 - T_c^4)$$

$$\text{where}\quad f = \frac{1}{\dfrac{1}{\varepsilon_c} + \dfrac{A_c}{A_w}\left(\dfrac{1}{\varepsilon_w} - 1\right)}$$

If $\varepsilon_c = 0.5$, $A_w \gg A_c$ and $\varepsilon_w = 0.1$ then Equation (3.17) yields:

$$\dot{Q}_{rad} = \varepsilon_c A_c \sigma (293^4 - 50^4)$$

$$\dot{Q}_{rad} = \varepsilon_c \times 41.7\ \mathrm{mW\,cm^{-2}}\ \text{for an unbaffled panel}$$

If $\varepsilon_c = 0.5$

$\dot{Q} = {\sim}190$ W for an area of 9000 cm^2

Single-stage cold heads are available with a refrigerating capacity of ~50 W at 50 K. This application would require four such heads (and associated He compressors). From the point of view of both temperature and pumping speed, this is not an appropriate application for a liquid-cryogen-based cryopump.

A possibility to reduce the number of cold heads/compressors would be to shield the 50 K panel with a LN_2-cooled baffle. This, however, would reduce S_{Xe} owing to transmission restrictions, thus requiring an equivalent increase in A_c. Further, the cost of a LN_2-cooled baffle and LN_2 have to be considered. An unexpected problem is that, at ~80 K, $p_{s,Xe}$ is ~ 10^{-2} mbar. If the sticking coefficient of Xe is significant then this may limit the minimum attainable pressure in the system.

Example 3.25

The cryopanel in a refrigerator-cooled cryopump is at $T_c = 14$ K. The pumping speed of the pump is 5000 L s^{-1} for N_2. The vapour pressures of various gas condensates are given in Table 3.8 at the applicable temperatures.

(a) What is the lowest partial pressure achievable by cryocondensation for N_2 and H_2?
(b) The cryopanel at 14 K is surrounded by an optically-tight baffle at 80 K, which reduces the pumping speed by a factor of 2. What is the conductance of the baffle for N_2?
(c) Estimate the area of the cryopanel (14 K) which would give an inlet pumping speed of 5000 L s^{-1} if the N_2 particles collide with the 80 K baffle before approaching the cryopanel.
(d) From Table 3.8, list those gases which would be pumped by the 80 K baffle to give a pressure below 10^{-6} mbar.

(a) $$p_{N_2} < 10^{-10}\,\text{mbar};\ p_{H_2} > 10\,\text{mbar (ca. 70 mbar)}$$

(b) $$S_{\text{eff}} = 5000\,\text{L s}^{-1} \quad \therefore \quad S_0 = 10^4\,\text{L s}^{-1}$$

Thus, from Equation (2.5):

$$C_{\text{baffle}} = 10^4\,\text{L s}^{-1}$$

(c) From equation (1.15) the area-related pumping speed:

$$S_A = \frac{\bar{c}}{4}\,\text{m}^3\,\text{s}^{-1}\,\text{m}^{-2}$$

For N_2 entering at 293 K:

$$S_{A,N_2} = 36.38\sqrt{\frac{293}{28}}\,\text{m}^3\,\text{s}^{-1}\,\text{m}^{-2}$$
$$= 11.77\,\text{L s}^{-1}\,\text{cm}^{-2}$$

For N_2 at 80 K:

$$S_{A,N_2} = 6.15\,\text{L s}^{-1}\,\text{cm}^{-2}$$

To achieve 10^4 L s^{-1}:

$$A_c = \frac{10^4\,\text{L s}^{-1}}{6.15\,\text{L s}^{-1}\,\text{cm}^{-2}}$$
$$\underline{= 1626\,\text{cm}^2}$$

(d) CO_2, H_2O

3.4 OTHER HIGH/ULTRA-HIGH VACUUM PUMPS

The remaining vacuum pumps to be discussed in this chapter fall into a group which remove gas particles from systems by sorption effects such as adsorption, chemisorption/gettering and implantation. They tend to be used on systems where any contamination of the vacuum by pump fluids, lubricants, *etc.* must be avoided. However, those pumps that remove gas particles exclusively by temperature-dependent gas adsorption on molecular sieves or Al_2O_3 (adsorption pumps) will not be discussed.

In high/UHV pumps where the pumping action is based on sorption effects, the removal of gas is brought about essentially by chemical reaction (gettering) at the surface of materials such as titanium. With some getter pumps, reactive metal surfaces are freshly generated during pump operation either by evaporation (as in titanium sublimation pumps) or by sputtering (as in sputter-ion pumps). With non-evaporable getter (NEG) pumps, the passive layer which is formed during reaction with gases such as O_2, N_2, H_2O, is removed by degassing in vacuum.

3.4.1 Sputter-ion Pumps (SIP)

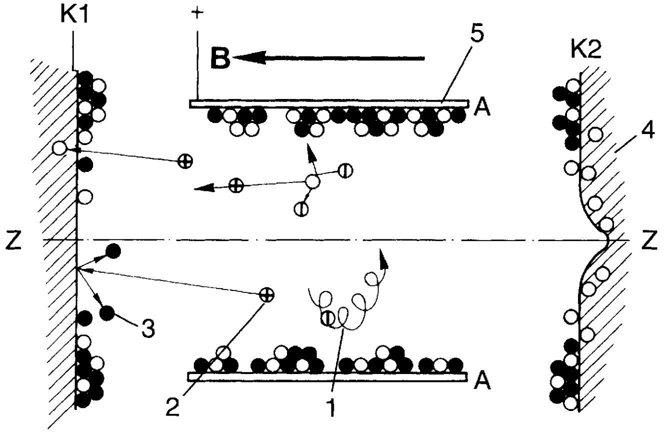
The pumping action of a SIP is based on sorption processes initiated by gas ions formed in a Penning discharge (see Chapter 5) maintained by a strong (flux density 0.1 to 0.2 T), homogeneous magnetic field. Ions impinge on parallel cathode plates made of a getter material such as Ti and sputter the getter which adheres to nearby surfaces within the pump and adsorbs reactive gases. Gas ions with sufficient energy will also implant themselves within the cathode. This is the process by which unreactive species such as noble gases are removed.

Example 3.26

The electrode system of a diode-type sputter-ion pump is shown in the diagram below.

(a) Identify items in the diagram marked A, B, K1 and K2 and 1–5.
(b) Briefly explain the pumping mechanism.

(a) A = anode (Penning cell); B = Magnetic flux line produced by a permanent magnet attached to the outside of the pump; K1, K2 = cathode plates (Ti in contact with the pump walls).
1 = electron (spiral track); 2 = ionised gas particles; 3 = sputtered Ti; 4 = implanted (buried) gas particle; 5 = gas particle incorporated into sputtered Ti.



(b) Ions generated in a Penning discharge (a sputter-ion pump can consist of a large number of such cells) impinge on the cathode plates and sputter Ti. The amount sputtered is roughly proportional to the pressure in the pump. This material adheres to the surfaces of the anode and between the sputtering regions of the opposite cathode and getters reactive gases. Some ionised particles have sufficient energy to penetrate well into the cathode (ion implantation). This mechanism of pumping is effective for all types of ion (including noble gases). However, as cathode sputtering proceeds, such particles are released giving rise to gas instabilities whereby the gas pressure increases significantly with a frequency of a few seconds or minutes. This effect reduces the noble gas pumping speed to about 1–3% of that for N_2. A significant increase in both the speed and stability for noble gas pumping is achieved with the so-called triode SIP (see Figure 3.12).

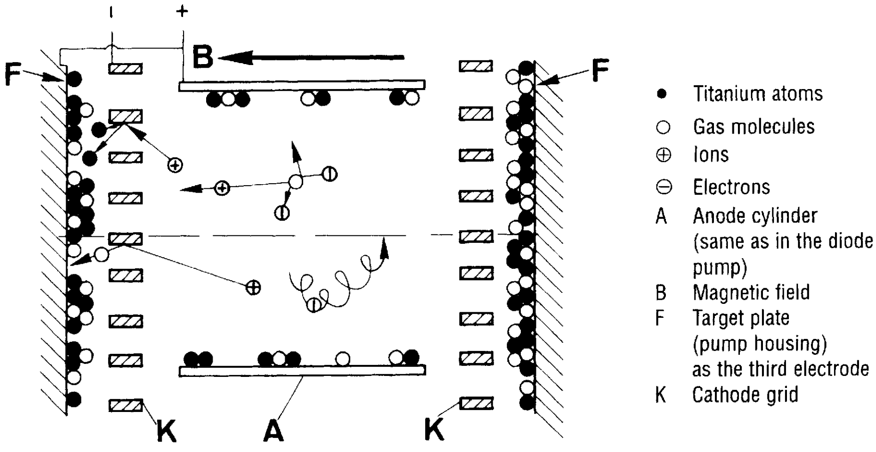


Figure 3.12 *Schematic diagram of the electrode system of a triode-type sputter ion pump*

In the triode-type SIP, the Ti cathode is in the form of a grid and behind this there is a collector (target) plate at anode potential. The greater efficiency for pumping noble gases is due to the fact that the geometry of the system favours grazing incidence of the ions from the discharge on the cathode grid. Compared to perpendicular incidence, this increases both the sputtering yield and the number of ions that are neutralised and reflected. The latter travel to the target plate with high energy and implant themselves but with negligible sputtering. Ions which are not neutralised cannot move against the electrical field between K and F and return towards K. Because sputtering is less at F, the re-emergence of implanted particles is much reduced. This results in an enhanced pumping speed for noble gases (20–30% S_{N_2}).

The pumping speed of a sputter-ion pump depends on the type of gas and the pressure. The $S(p)$ curve is mainly determined by the discharge conditions and it reaches a flattish maximum around 10^{-6} mbar.

The nominal pumping speed of a sputter-ion pump is given by the maximum in the pumping speed curve for air (the corresponding pressure must be stated).

For air, N_2, CO_2 and $H_2O(v)$, S is about the same. S, relative to S_{air} for other gases for a triode pump is given in Table (3.9).

Table 3.9 *Pumping speed of a triode SIP for a range of gases compared to* S_{air}

Gas	*Relative pumping speed*
H_2[a]	140–150%
H_2O	80%
CH_4	100%
Other light hydrocarbons	60–120%
O_2	80%
Ar	25%
He	30%

[a] At $p < 5 \times 10^{-6}$ mbar

H. Henning, in ref. (f), p. 317.

Continuous use of SIPs is restricted at pressures exceeding 10^{-4} bar (owing to cathode heating and degassing). They can be switched on at a starting pressure, the rule of thumb for which is:

$$p_{\text{start}} = (0.01\text{–}0.02)\,\frac{S}{V} \tag{3.22}$$

when p is in mbar; S is in L s^{-1}; V is in L.

This expression is satisfactory for triode pumps but should be reduced by a factor of 10 for diode pumps.

Example 3.27

A gas stream (10^{-6} Pa m^3 s^{-1}) consisting of 10% H_2 in Ar is admitted to a small chamber connected to a triode SIP with a pumping speed for air of 10 L s^{-1}. Estimate the total pressure in the system.

$$10^{-6}\,\mathrm{Pa\,m^3\,s^{-1}} \equiv 10^{-5}\,\mathrm{mbar\,L\,s^{-1}}$$

According to Table 3.9, for triode SIPs:

$$\begin{aligned}
S_{H_2} &= (140\text{–}150\%)\,S_{air} = 14\text{–}15\,\mathrm{L\,s^{-1}} \\
S_{Ar} &= 25\%\,S_{air} \qquad\quad = 2.5\,\mathrm{L\,s^{-1}} \\
p_{tot} &= p_{H_2} + p_{Ar} \\
&= \frac{q_{H_2}}{S_{H_2}} + \frac{q_{Ar}}{S_{Ar}} = \frac{10^{-6}\,\mathrm{mbar\,L\,s^{-1}}}{(14\text{–}15\,\mathrm{L\,s^{-1}})} + \frac{9\times10^{-6}\,\mathrm{mbar\,L\,s^{-1}}}{2.5\,\mathrm{L\,s^{-1}}} \\
&= (7.1\text{–}6.75)\times10^{-8}\,\mathrm{mbar} + 3.6\times10^{-6}\,\mathrm{mbar} \\
&\cong \underline{3.7\times10^{-6}\,\mathrm{mbar}}
\end{aligned}$$

Example 3.28

A chamber is fitted with a triode SIP with S_{air} = 100 L s^{-1}. A gas mixture containing 5% CH_4 + 10% O_2 in N_2 is admitted. If a total pressure in the chamber of 10^{-6} mbar is required, calculate the flow-rate of the gas mixture if all other gas sources can be neglected.

$$\begin{aligned}
p_{tot} &= p_{CH_4} + p_{O_2} + p_{N_2} = 1\times10^{-6}\,\mathrm{mbar} \\
&= \frac{q_{CH_4}}{S_{CH_4}} + \frac{q_{O_2}}{S_{O_2}} + \frac{q_{N_2}}{S_{N_2}} \\
&= \frac{5\times10^{-2}q_{tot}}{S_{CH_4}} + \frac{0.1q_{tot}}{S_{O_2}} + \frac{0.85q_{tot}}{S_{N_2}}
\end{aligned}$$

$$S_{N_2} = S_{air}$$

$$S_{O_2} = 0.8S_{air}$$

$$S_{CH_4} = S_{air}$$

$$\begin{aligned}
\therefore\quad 1\times10^{-6}\,\mathrm{mbar} &= 5\times10^{-4}q_{tot} + 1.25\times10^{-3}q_{tot} + 8.5\times10^{-3}q_{tot} \\
&= 10.25\times10^{-3}\,\mathrm{L\,s^{-1}}q_{tot}\,\mathrm{mbar}
\end{aligned}$$

$$\therefore\quad q_{tot} = 9.76\times10^{-5}\,\mathrm{mbar\,L\,s^{-1}}$$

Example 3.29

A spherical UHV chamber has a volume of 15 L and is to be pumped down to 10^{-8} mbar in 12 h with a diode SIP. The gas load (mainly water vapour) after 12 h has been estimated as 1.2×10^{-6} mbar L s^{-1}.

(a) Calculate the required pumping speed of the SIP.
(b) Calculate the maximum pressure at which the SIP can be started.
(c) If the only available pump to evacuate the chamber to the SIP starting pressure is a two-stage oil-sealed rotary pump, what precautions should be taken?

(a) According to Equation (2.7),

$$S_{\text{eff}} = \frac{q_{pV}}{p}$$

$$\therefore \quad S_{\text{eff}} = \frac{1.2 \times 10^{-6}\,\text{mbar L s}^{-1}}{1 \times 10^{-8}\,\text{mbar}}$$

$$= \underline{120\,\text{L s}^{-1}}$$

(b) According to Equation (3.22),

$$p_{\text{start}} = (0.01\text{–}0.02)\frac{S}{V}\,\text{mbar} \quad \text{for a triode pump}$$

$$= (0.01\text{–}0.02) \times \frac{120}{15} \times 0.1 \quad \text{for a diode pump}$$

$$= \underline{8 \times 10^{-3} \text{ to } 2 \times 10^{-2}\,\text{mbar}}$$

A pressure below 8×10^{-3} mbar would be preferred because switching on the pump at 10^{-2} mbar would initiate a glow discharge which, with a diode pump, would exist throughout the pump housing since the pump wall is at cathode potential. This discharge can even spread into the chamber being pumped.

(c) To ensure cleanliness in the system, oil vapour must be prevented from entering both the UHV chamber and the diode SIP. The latter type of pump is strongly affected by oil and when contaminated, starts up slowly and has a reduced S. It would be recommended to valve off the SIP when it is not in use and to provide the oil-sealed pump with a foreline adsorption trap or catalytic combustion device.

3.4.2 Getter Pumps

3.4.2.1 Titanium Sublimation Pumps. These are fairly simple devices consisting of a stainless steel pump body containing the evaporation source and, usually, a screen collector for the evaporated material (ref. (g)). They exploit the adsorption of chemically-active gases at the surface of the getter film. The characteristics of adsorption are frequently expressed in terms of the sticking probability (s) as a function of surface coverage (often expressed in particles cm^{-2}). Depending on gas type, when one or more monolayers have been formed, the sorption speed falls rapidly and a new surface must be formed by further evaporation.

The sorption characteristics of Ti are dependent on the deposition temperature of the getter film. Good results are obtained by deposition at 77 K because the film formed is more porous (*i.e.* has a higher surface area) than those formed at, say, room temperature.

Sticking probabilities as a function of monolayer formation are given in Table 3.10.

Table 3.10 *Sticking probabilities (s) for various gases on Ti films at 77 K and 300 K as a function of coverage (θ)*

Gas	*Coverage* (θ)					
	0.5		1		2	
	s(77)	*s(300)*	*s(77)*	*s(300)*	*s(77)*	*s(300)*
O_2	1.0	0.8–1.0	1	1	0.8	0.9
N_2	0.7–1.0	0.3	0.005	0.003	—	—
H_2	0.2–0.4	0.01–0.06	0.03	0.02	—	—
CO	0.95–1.0	0.7–1.0	0.8	0.2	0.1	—
CO_2	—	0.5	—	—	—	—

Data taken from ref. (d), p. 269, B. Ferrario, in ref. (f), p. 294.

Where gases are simultaneously pumped, some can displace others. Gupta and Leck (*Vacuum*, 1975, **25**, 562) found that O_2 can displace all other gases, CO can displace CH_4, N_2 and H_2, and H_2 can displace N_2 and CH_4.

Example 3.30

The collecting screen inside a TSP is 14 cm in diameter and 18 cm in length. In addition, at the base, there is a circular plate of the same diameter as the screen and cooled by heat conduction.

(a) If the screen is cooled to 77 K and covered with a fresh Ti layer, calculate the pumping speed for N_2 at 20 °C.

(b) If the inlet to the pump is DN125 but all the other conditions are the same, calculate the speed of the pump at the inlet.

(Based on Example 8.10, p. 298, ref. (d′) with permission.)

From Equation (1.17) and (1.18) the volumetric flow of gas onto a wall (area = A) is:

$$q_V = \frac{A\bar{c}}{4}$$

For a getter surface with a sticking probability (s), the pumping speed (S) is:

$$S_0 = sq_V = \frac{sA\bar{c}}{4} \tag{3.23}$$

(a) For N_2, the sticking probability for Ti at 77 K is, according to Table 3.10, 0.7 to 1.0 (say 1.0). The area (A) of the collecting screen is:

$$\begin{aligned} A &= \frac{\pi d^2}{4} + \pi dl \\ &= \frac{\pi(14)^2}{4} + (\pi \times 14 \times 18\,\text{cm}^2) \\ &= 154 + 792\,\text{cm}^2 \\ &= 946\,\text{cm}^2 \end{aligned}$$

$$S_0 = 1.0 \times 946\,\text{cm}^2 \times \frac{\bar{c}}{4}\,\text{L s}^{-1}$$

From Example 1.9:

$$\bar{c} = 145.5\sqrt{\frac{T}{M}}\,\text{m s}^{-1}$$

$$\therefore \quad \frac{\bar{c}}{4} = 117.7\,\text{m s}^{-1}$$

So

$$S = 11.8\,\text{L s}^{-1}\,\text{cm}^{-2}$$

$$\therefore \quad S_0 = 11.8\,\text{L s}^{-1}\,\text{cm}^{-2} \times 946\,\text{cm}^2$$

$$= \underline{11\,163\,\text{L s}^{-1}}$$

(b) If the pump opening is DN125 (127 mm), its conductance for N_2 is given by $A\bar{c}/4$ (Equation 2.22):

$$\begin{aligned} \therefore\quad C_{\text{ap}} &= 11.8\ \text{L s}^{-1}\,\text{cm}^{-2} \times A_{\text{ap}}\,\text{cm}^2 \\ &= 11.8\ \text{L s}^{-1}\,\text{cm}^{-2} \times 127\ \text{cm}^2 \\ &= 1499\ \text{L s}^{-1} \end{aligned}$$

$$\begin{aligned} \frac{1}{S_{\text{eff,TSP}}} &= \frac{1}{S_0} + \frac{1}{C_{\text{ap}}} \\ &= \frac{C_{\text{ap}} + S_0}{S_0 C_{\text{ap}}} \\ \therefore\quad S_{\text{eff,TSP}} &= \frac{S_0 C_{\text{ap}}}{C_{\text{ap}} + S_0} = \frac{11\,163\ \text{L s}^{-1} \times 1499\ \text{L s}^{-1}}{(1499 + 11\,163)\ \text{L s}^{-1}} \\ &= \underline{\underline{1322\ \text{L s}^{-1}}} \end{aligned}$$

Example 3.31

N_2 molecules (radius = 1.84×10^{-10} m) are adsorbed on the surface of a Ti layer. Assuming that they are hexagonally close-packed, calculate the amount of N_2 (in units of mbar L) adsorbed per unit area of the Ti.

The area of the base of a unit cell of hcp spheres of radius r is $2\sqrt{3}r^2$. If N_2 molecules are spherical then the area (A) of the base of a unit cell of N_2 molecules is:

$$\begin{aligned} A &= 2\sqrt{3} \times (1.84 \times 10^{-10})^2\ \text{m}^2 \\ &= 1.17 \times 10^{-19}\ \text{m}^2 \end{aligned}$$

The number of N_2 molecules occupying 1 m^2 of surface as a monolayer is:

$$\frac{1}{A} = 8.5 \times 10^{18}$$

$$\sim 10^{19}\ \text{molecules}$$

$$\text{As}\quad N_{\text{A}} = 6.022 \times 10^{23}\ \text{mol}^{-1}$$

the amount of adsorbed gas

$$= 1.6 \times 10^{-5}\ \text{mol m}^{-2}$$

$$pV = nRT$$

For 1 mole:

$$\begin{aligned} pV &= RT \\ &= 83.14\,\text{mbar L mol}^{-1}\,\text{K}^{-1} \times T\,(\text{K}) \end{aligned}$$

At 273 K:

$$pV = 2.27 \times 10^4\,\text{mbar L mol}^{-1}$$

Amount of adsorbed N_2

$$\underline{= 0.36\,\text{mbar L (m}^{-2}\text{ of monolayer)}}$$

Example 3.32

In Example 3.30, the inlet speed of the TSP was calculated as 1322 L s^{-1} based on a Ti surface area of 946 cm^2. If the TSP is working at 10^{-8} mbar, N_2, calculate how long it will take to cover the Ti with a monolayer.

$$\begin{aligned} q_{in,TSP} &= p_{\text{in}} \times S_{\text{eff}} \\ &= 10^{-8}\,\text{mbar} \times 1322\,\text{L s}^{-1} \\ &= 1.32 \times 10^{-5}\,\text{mbar L s}^{-1} \end{aligned}$$

From Example 3.31, the amount of N_2 required to form a monolayer on 946 cm^2 Ti is:

$$0.36\,\text{mbar L m}^{-2} \times 0.0946\,\text{m}^2 = 0.034\,\text{mbar L}$$

$$\therefore \quad \underline{\text{time for monolayer formation is 2580 s}}$$

Example 3.33

Given the radius of an adsorbed H_2 molecule is 1.2×10^{-10} m and H_2 adsorbs on Ti in a hexagonally close-packed layer, calculate the length of time that will result in the coverage of 946 cm^2 of freshly deposited Ti at 300 K with half a monolayer of H_2 if a TSP is working at 10^{-7} mbar at 300 K.

Working as for Example 3.31:

$$\begin{aligned} A_{H_2,\text{ads}} &= 2\sqrt{3}(1.2 \times 10^{-10})^2\,\text{m}^2 \\ &= 5 \times 10^{-20}\,\text{m}^2 \end{aligned}$$

$\therefore$ Number of molecules m^{-2}

$$\begin{aligned} &= \frac{1}{5 \times 10^{-20}} \\ &= 2 \times 10^{19} \end{aligned}$$

Amount of H_2 per m^2 of Ti surface

$$= \frac{2 \times 10^{19}}{N_A}$$
$$= 3.3 \times 10^{-5}\,\text{mol}$$

As in Example 3.31, but at 300 K:

$$pV = 2.49 \times 10^4\ \text{mbar L mol}^{-1}$$

Amount of adsorbed H_2

$$= 3.3 \times 10^{-5}\,\text{mol m}^{-2} \times 2.49 \times 10^4\text{mbar L mol}^{-1}$$
$$= 0.82\,\text{mbar L adsorbed on Ti}$$

For 0.5 ML (monolayer):

$$\text{Amount} = 0.41\ \text{mbar L m}^{-2}$$
$$= 0.039\,\text{mbar L adsorbed on }946\,\text{cm}^2\ \text{Ti}$$

Based on 946 cm^{2}of freshly-deposited Ti at 300 K:

$$S_0 = \frac{sA\bar{c}}{4}$$

From Table 3.10, s (300 K) = 0.01–0.06 (dependent on experimental conditions). Using the expression for $\bar{c}$ in Example 1.9, $\bar{c}_{\,H_2,300K} = 1782\,\text{m s}^{-1}$

$$\therefore \quad S_0 = (0.01\text{–}0.06) \times 946\,\text{cm}^2 \times 44.5\ \text{L s}^{-1}\ \text{cm}^{-2}$$
$$= (420\text{–}2526)\ \text{L s}^{-1}$$

For H_2 at 300 K,

$$C_{ap} = \frac{A\bar{c}}{4}$$
$$= 127\,\text{cm}^2 \times 44.5\ \text{L s}^{-1}\ \text{cm}^{-2}$$
$$= 5652\ \text{L s}^{-1}$$

$$S_{eff} = \frac{S_0 C_{ap}}{C_{ap} + S_0}\ \text{L s}^{-1}$$
$$= 387\text{–}1725\ \text{L s}^{-1}$$

∴ q_{pV,H_2} at 10^{-7} mbar = 3.87×10^{-5} mbar L s^{-1}–1.73×10^{-4} mbar L s^{-1}

∴ Adsorption time for half a monolayer = $\underline{930\text{–}210\ \text{s}}$

Actually, it is likely that adsorbed H_2 will not remain at the surface but diffuse into the interior so that the surface coverage may remain low ($\theta < 0.5$) for a much longer time than that predicted.

CHAPTER 4

Gas Sources and Attainable Pressure in Vacuum Systems

4.1 INTRODUCTION

It is impossible to eliminate all sources of gas in vacuum systems. Even in the best-designed and operated static systems at very low pressure, small leaks are present and slight outgassing occurs, and the resulting gas load has to be dealt with by the system's pumps. The usual sources of gas are indicated in Figure 4.1, and some general comments should be made before more detailed discussion in later sections.

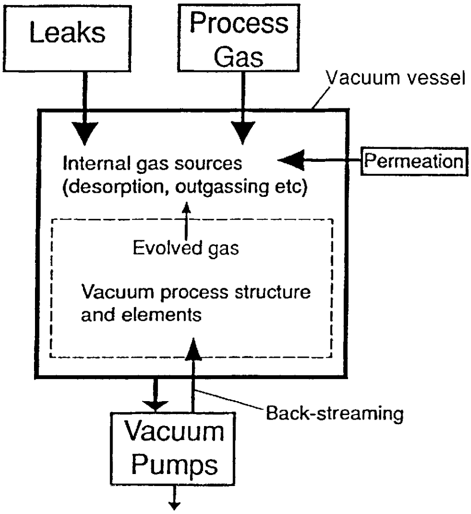


Figure 4.1 *Gas sources in vacuum systems*

1 *Leaks*. No system can be free of leaks but leakage must be reduced to the extent that it no longer adversely affects the performance of the vacuum system.

2 *Outgassing.* Any material that has been exposed to gas, particularly atmospheric air, will adsorb or otherwise entrap that gas. Under reduced pressure, not only do the inner walls and associated components contribute to the gas load but also any substrates or material being processed.

3 *Permeation.* The metals and alloys normally used in vacuum systems can be regarded as impermeable to air even at high temperatures. In some circumstances, however, the permeation of H_2, He, O_2, air, *etc.* through elastomers, glasses and some metals must be considered.

4 *Process gas.* In, for example, flow-reactors, sputtering systems and systems with flowing purge gas, gas is deliberately introduced. In such cases, the pumping system must deal with this gas load, in addition to 1–3 above, to maintain the pressure.

4.2 LEAKS

A leak is a flow path in the boundary of a system that allows a fluid to pass from a region at one pressure to one at a lower pressure. Generally, with vacuum systems, leaks introduce ambient air, thereby impairing the performance of the system and causing severe problems with air-sensitive materials and processes. Leaks are often subdivided into 'real' and 'virtual' leaks. A 'real' leak may exist because of cracking in polycrystalline materials as a result of strain in a component. It may also arise because of careless handling of components, leading to radial scratches on flange surfaces or the contamination of gaskets, O-rings, *etc.* They can also arise through misuse, ageing or thermal degradation of seals. 'Virtual' leaks arise from trapped volumes within a vacuum chamber. The term is often also applied to the emission of gas from the internal walls of a system on the components contained in the system (see Section 4.3).

The flow of material through a leak can generally be described by the equations of flow described in Chapter 2. In reality, however, the leak may be a tortuous path of ill-defined length and diameter in which the nature of the gas flow is imprecise. Nevertheless, some estimates of leakage based on 'model' systems give an idea of the amount of leakage which occurs through a leak of a given size.

Example 4.1

A human hair is trapped across an O-ring on a vacuum system where the internal pressure is 10^{-4} mbar and the external pressure is 10^{3} mbar. The temperature is 20 °C. Leakage of air into the vacuum system is occurring.

(a) If the trapped hair is a leak that can be regarded as a uniform tube of 70 μm diameter (the approximate diameter of a human hair) and length = 8 mm (see Example 4.22) with the above pressures at the exit and entrance, respectively, what is the nature of the gas flow across the leak?
(b) Estimate the leakage (q_L).

(a) The type of flow can be determined by *Kn* (Equation 1.28).
From Table 1.2, for air at 20 °C:

$$\bar{l}p = 6.5 \times 10^{-5}\,\text{m mbar}$$
$$= 6.5 \times 10^{-3}\,\text{cm mbar}$$

At the leak inlet, $p = 10^3$ mbar

$$\therefore \bar{l} = 6.5 \times 10^{-6}\,\text{cm}$$

As $d = 70\,\mu\text{m}\ (7 \times 10^{-3}\,\text{cm})$,

$$Kn = \frac{\bar{l}}{d}$$
$$= \frac{6.5 \times 10^{-6}\,\text{cm}}{7 \times 10^{-3}\,\text{cm}}$$
$$= 9.3 \times 10^{-4}$$

As $Kn \ll 0.01$, viscous flow will predominate.
At the leak outlet, $p = 10^{-4}$ mbar:

$$\therefore \quad \bar{l} = 65\,\text{cm}$$
$$\therefore \quad Kn = 9286$$

i.e. molecular flow would predominate and no uniform flow would be established across the leak.

(b) If it is assumed that viscous, laminar flow of air occurs in the leak then, according to Equation (2.14):

$$q_L = 135\frac{d^4}{l}\left(\frac{p_{\text{ext}}^2 - p_{\text{vac}}^2}{2}\right)\text{mbar L s}^{-1}$$

As $p_{\text{vac}} \ll p_{\text{ext}}$,

$$= \frac{135 \times (7 \times 10^{-3})^4}{0.8}\left(\frac{1000^2}{2}\right)\text{mbar L s}^{-1}$$
$$= \underline{0.2\,\text{mbar L s}^{-1}}$$

It is probable that, at the leak exit, because the pressure is so low, choked flow will be established. For air at 20 °C, the critical pressure (p^*) at which this is established is given by Equation (2.17):

$$p^* = 2.3\frac{d^2}{l}p_{\text{ext}}^2$$

In this case:

$$p^* = 2.3 \times \frac{(7 \times 10^{-3})^2}{0.8} \times 1000^2\,\text{mbar}$$

$$= 140.9\,\text{mbar}$$

The pV throughput under choked flow conditions is given by Equation (2.18):

$$q_L = 135\frac{d^4}{l}\frac{(p_{\text{ext}}^2 - p^{*2})}{2}\,\text{mbar L s}^{-1}$$

$$= 0.198\,\text{mbar L s}^{-1}$$

$$\underline{\sim 0.2\,\text{mbar L s}^{-1}}$$

This is almost identical to the above value, therefore choked flow can be ignored.

If it is assumed that molecular flow occurs in the leak then, according to Equation (2.37):

$$C_{\text{leak}} = \frac{12.1d^3}{l}\,\text{L s}^{-1}$$

with $d = 7 \times 10^{-3}$ cm and $l = 0.8$ cm

$$C_{\text{leak}} = 5.19 \times 10^{-6}\,\text{L s}^{-1}$$

$$q_L = C_{\text{leak}} \times (p_{\text{ext}} - p_{\text{vac}})$$

$$= 5.2 \times 10^{-3}\,\text{mbar L s}^{-1}$$

The actual air in-leakage is between 0.2 and 5.2×10^{-3} mbar L s^{-1}, according to the above.

(*Note*: In the authors' experience, it is nearer the lower value.)

Example 4.2

A leak in a vacuum chamber can be considered to be a cylindrical pore with a diameter of 3 μm and length 2 mm. If the external pressure is 10^3 mbar and internally there is a 'vacuum' (p internally is negligibly small), calculate the air in-leakage (q_L) at 20 °C.

As in Example 4.1, $\bar{l}p$ (air) $= 6.5 \times 10^{-5}$ m mbar.

At the high pressure side of the leak:

$$\bar{l} = 6.5 \times 10^{-8}\ \text{m}$$

$$\text{as } d = 3 \times 10^{-6}\ \text{m}$$

$$\frac{\bar{l}}{d} \cong Kn = 2.2 \times 10^{-2}\ \text{(viscous flow)}$$

If it is assumed that viscous, laminar flow predominates:

$$q_L = 135 \frac{d^4}{l}\left(\frac{p_{\text{ext}}^2 - p_{\text{int}}^2}{2}\right)\text{mbar L s}^{-1}$$

Since $p_{\text{ext}} = 10^3$ mbar

and $p_{\text{int}} = 0$

$$\underline{q_L = 2.7 \times 10^{-6}\ \text{mbar L s}^{-1}}$$

Since leaks cannot be eliminated in vacuum systems, it is necessary to establish a leakage limit. A practical expression of this is that leakage should not exceed 10% of the minimum throughput for the system or:

$$\begin{aligned} q_{\text{leak,tot}} &\le 0.1\, q_{pV,\text{min,system}} \\ &\le 0.1\, p_{\text{base}} \times S_{\text{eff}} \text{ at } p_{\text{base}} \end{aligned} \tag{4.1}$$

Example 4.3

A system at 20 °C has to achieve 10^{-9} mbar after prolonged pumping with a turbomolecular pump ($S_{\text{eff}} = 300$ L s^{-1}, independent of gas type). What is the maximum allowable leakage?

From Equation (4.1):

$$\begin{aligned} q_{leak,tot} &\le 0.1\, p_{\text{base}} \times S_{\text{eff}} \\ \therefore\quad q_{\text{max}} &= 0.1 \times 10^{-9}\ \text{mbar} \times 300\ \text{L s}^{-1} \\ &= \underline{3 \times 10^{-8}\ \text{mbar L s}^{-1}} \end{aligned}$$

Note: If there are n leaks of equal leakage rate, an individual leak should not exceed q_{max}/n.

Leakage rates are generally expressed in units of pV throughput (see Equation 2.2 and comments). Mass flow rate (Equation 2.1) and molar flow rates (Equation 2.4) can also be used. Conversion factors for leak rates ($q_{pV,\text{leak}}$) and mass flow rates are often given for gases in their standard states (p_n, T_n). In practice, the difference between room temperature and T_n is not significant when compared to the uncertainties that can occur in the measurement of leakage.

Example 4.4

A system has air in-leakage totalling $5 \times 10^{-4}\,\text{mbar L s}^{-1}$ at 20 °C. Calculate (a) the amount of leakage expressed in normal cm³ per minute (b) the leakage in kg h⁻¹.

(a) p_n (normal atmospheric pressure) = 1013.25 mbar

$$\text{At } p_n,\quad q_{pV,20\,°\text{C}} = \frac{5 \times 10^{-4} \times 10^3}{1013.25}\,\text{cm}^3\,\text{s}^{-1}$$

$$= 4.93 \times 10^{-4}\,\text{cm}^3\,\text{s}^{-1}$$

$$\underline{= 2.96 \times 10^{-2}\,\text{cm}^3\,\text{min}^{-1}}$$

(b)

$$q_{pV} = p\dot{V} = \dot{m}\frac{RT}{M}$$

$$\therefore \quad \dot{m} = \frac{(p\dot{V}) \times M}{RT}$$

$$= \frac{5 \times 10^{-4}\,\text{mbar L s}^{-1} \times 29\,\text{g gmol}^{-1}}{83.14\,\text{mbar L gmol}^{-1}\,\text{K}^{-1} \times 293\,\text{K}}$$

$$= 5.95 \times 10^{-7}\,\text{g s}^{-1}$$

$$\underline{= 2.14 \times 10^{-6}\,\text{kg h}^{-1}}$$

The typical indication of a leak in a vacuum system is the inability of the system to achieve the usual base pressure even after prolonged pumping. Before carrying out an actual leak test using a search gas, the order of magnitude of any gas sources (including leakage) should be established. For this purpose, a pressure-rise test is useful. After evacuation, the system is isolated from its pumps. For a volume, V, initially at a pressure p but rising by an amount Δp over a length of time Δt, the amount of gas initially in the system (pV) changes by $\Delta(pV)$. This is equal to the amount of gas, q_{tot}, but it is frequently assumed to be the leakage q_L, taking place in time t:

$$\Delta(pV) = q_L\,\Delta t$$

For a chamber with a constant volume, V:

$$\Delta(pV) = V\Delta p$$

and

$$q_L = V\frac{\Delta p}{\Delta t} \tag{4.2}$$

Example 4.5

A diffusion-pumped vacuum system with a chamber volume of 0.75 m^3 is isolated from its pumps. The pressure increases from 2×10^{-3} mbar to 5×10^{-1} mbar in 10 minutes.

(a) What is the leakage rate, assuming no other gas sources.
(b) After repairing a significant leak, the system could be evacuated to 5×10^{-5} mbar with the diffusion pump ($S_{\text{eff}} = 2000\ \text{L s}^{-1}$). What leakage remains?

(a) From Equation (4.2):

$$q_L = V\frac{\Delta p}{\Delta t}$$

$$= \frac{750\ \text{L} \times 0.498\ \text{mbar}}{600\ \text{s}}$$

$$= \underline{0.62\ \text{mbar L s}^{-1}}$$

(b)

$$p = \frac{q_{\text{in}}}{S_{\text{eff}}}$$

$$\therefore \quad q_{\text{in}} = 5 \times 10^{-5}\ \text{mbar} \times 2 \times 10^{3}\ \text{L s}^{-1}$$

$$= \underline{0.1\ \text{mbar L s}^{-1}}$$

Example 4.6

The total leakage on a system ($V = 20$ L) is 10^{-7} mbar L s^{-1}. If the system is isolated from its pumps at $p = 1 \times 10^{-5}$ mbar, how long will it take before the pressure has increased to 10^{-3} mbar? (Assume no other gas sources except leaks.)

$$q_L = V\frac{\Delta p}{\Delta t}$$

$$\therefore \ \Delta t = V \times \frac{\Delta p}{q_L}$$

$$= \frac{20\,\text{L} \times 99 \times 10^{-5}\,\text{mbar}}{10^{-7}\,\text{mbar L s}^{-1}}$$

$$\underline{= 198\,000\,\text{s}\ (55\,\text{h})}$$

The calculated value for q_L based on a pressure-rise test (Equation 4.2) may not be solely due to leaks. Depending on the pressure range involved, 'virtual' gas sources will also be involved.

To determine whether the pressure rise is due to leakage only, it must be repeated in different pressure ranges. If, at starting pressures $<10^{-1}$ mbar, a rapid pressure increase is observed which decreases with increasing pressure, eventually levelling off before atmospheric pressure is reached, this indicates outgassing/evaporation. If $\Delta p/\Delta t$ remains constant up to pressure of 10s or 100s of mbar, leakage is taking place. In practice, both outgassing and leakage occur simultaneously.

Example 4.7

A stainless steel high vacuum system ($V = 15$ L) has been pumped for 36 h and the pressure is 1×10^{-7} mbar. A pressure-rise test, starting at 10^{-5} mbar, shows a pressure of 1.5×10^{-3} mbar after 20 min. Calculate the amount of gas entering the chamber and comment on the source of the gas.

$$\begin{aligned}
\text{Pressure rise } (\Delta p) &= (1.5 \times 10^{-3} - 1 \times 10^{-7})\,\text{mbar} \\
&= 1.5 \times 10^{-3}\,\text{mbar} \\
\Delta t &= 20 \times 60\,\text{s} \\
\therefore\quad q_{\text{gas}} &= V\frac{\Delta p}{\Delta t} \\
&= 15 \times \left(\frac{1.5 \times 10^{-3}}{1200\text{s}}\right) \\
&= \underline{1.9 \times 10^{-5}\,\text{mbar L s}^{-1}}
\end{aligned}$$

After 36 h pumping, the amount of outgassing from the walls of a clean chamber of this volume ($S \cong 0.3\,\text{m}^2$ for a spherical chamber) should be low compared to leakage (see Section 4.3). It is likely, therefore, that this pressure rise is due predominantly to air in-leakage.

If pressure-rise measurements indicate that a search for a leak is worthwhile then it is likely that helium will be used as a search gas and a commercial mass-spectrometer leak detector (MSLD) will be used as a selective helium detector. In practice, with a leaking system, air in-leakage is of concern. If helium is used as a search gas, the indicated leakage will be different to the air in-leakage. Depending on the nature of gas flow in a leak, the relationships between the leak rates for different gases (assuming identical temperatures) are given by the expressions:

For viscous, laminar flow:

$$\frac{q_{\mathrm{L,gas\,1}}}{q_{\mathrm{L,gas\,2}}} = \frac{\eta_{\mathrm{gas\,2}}}{\eta_{\mathrm{gas\,1}}} \tag{4.3}$$

where η = dynamic viscosity.

For molecular flow:

$$\frac{q_{\mathrm{L,gas\,1}}}{q_{\mathrm{L,gas\,2}}} = \sqrt{\frac{M_{\mathrm{gas\,2}}}{M_{\mathrm{gas\,1}}}} \tag{4.4}$$

where M = relative molar mass.

Example 4.8

A vacuum chamber has a leak which can be considered to be a cylindrical pore with $d = 3\ \mu\mathrm{m}$ and $l = 4\,\mathrm{mm}$.

(a) If the external pressure is 10^3 mbar and, internally, there is a pressure of 10^{-4} mbar, calculate the leakage (q_L) for air at 20 °C.

(b) Calculate the amount of leakage if the chamber was surrounded by He under identical conditions.

(a) As stated in Example 4.1, leakage can be calculated having established the flow type. At the leak inlet, $\bar{l}_{\mathrm{air}} = 6.5 \times 10^{-6}$ cm (cf. Example 4.1). With $d = 3 \times 10^{-4}$ cm, $Kn = 2.2 \times 10^{-2}$.

If viscous, laminar flow predominates in the leak then, according to Equation (2.14):

$$q_{\mathrm{L,air}} = 135\frac{d^4}{l}\left(\frac{p_{\mathrm{ext}}^2 - p_{\mathrm{vac}}^2}{2}\right)\mathrm{mbar\,L\,s^{-1}}$$

As p_{vac} is negligible compared to p_{ext}:

$$q_{\mathrm{L,air}} = \frac{135\,(3 \times 10^{-4})^4}{0.4}\left(\frac{1000^2}{2}\right)\mathrm{mbar\,L\,s^{-1}}$$

$$\underline{= 1.37 \times 10^{-6}\,\mathrm{mbar\,L\,s^{-1}}}$$

Again, as shown in Example 4.1, molecular flow would predominate at the leak outlet.

Under these conditions:

$$C_{\text{leak}} = 12.1\,\frac{d^3}{l}\ \text{L s}^{-1}$$

$$= 8.2 \times 10^{-10}\ \text{L s}^{-1}$$

$$\underline{q_{\text{L,air}} = 8.2 \times 10^{-7}\ \text{mbar L s}^{-1}}$$

The actual leakage would be between these extreme values.

(b) For viscous laminar flow, from Equation (4.3):

$$\frac{q_{\text{L,air}}}{q_{\text{L,He}}} = \frac{\eta_{\text{He}}}{\eta_{\text{air}}}$$

At 20 °C (see Table 1.3):

$$\eta_{\text{He}} = 19.6 \times 10^{-6}\ \text{kg m}^{-1}\,\text{s}^{-1}$$
$$\eta_{\text{air}} = 18.2 \times 10^{-6}\ \text{kg m}^{-1}\,\text{s}^{-1}$$

With He entering,

$$q_{\text{L,He}} = \frac{q_{\text{L,air}} \times \eta_{\text{air}}}{\eta_{\text{He}}}$$

$$= 1.37 \times 10^{-6}\ \text{mbar L s}^{-1} \times \frac{18.2 \times 10^{-6}\ \text{kg m}^{-1}\,\text{s}^{-1}}{19.6 \times 10^{-6}\ \text{kg m}^{-1}\,\text{s}^{-1}}$$

$$= 1.37 \times 10^{-6}\ \text{mbar L s}^{-1} \times 0.93$$
$$\underline{= 1.27 \times 10^{-6}\ \text{mbar L s}^{-1}}$$

For molecular flow, from Equation (4.4):

$$\frac{q_{\text{L,air}}}{q_{\text{L,He}}} = \sqrt{\frac{M_{\text{He}}}{M_{\text{air}}}}$$

$$\therefore\quad q_{\text{L,He}} = q_{\text{L,air}}\sqrt{\frac{M_{\text{air}}}{M_{\text{He}}}}$$

$$= 8.2 \times 10^{-7}\ \text{mbar L s}^{-1} \times 2.7$$
$$\underline{= 2.2 \times 10^{-6}\ \text{mbar L s}^{-1}}$$

Example 4.9

A component is attached to a vacuum system ($V = 100$ L) *via* an isolation valve. The free volume of the component and its connection to the valve is $40\,\text{cm}^3$. With the valve open, the base pressure in the system and the component is 10^{-6} mbar. The component has a leak of 2×10^{-5} mbar L s^{-1}

(a) If the valve to the system is closed for an hour, what pressure will be established in the component?
(b) If the system's pumps are isolated and then the valve opened quickly, to what level will the pressure increase?

(a) If the component is isolated at a pressure of 1×10^{-6} mbar, the amount of gas initially present $= 0.04\,\text{L} \times 10^{-6}\,\text{mbar}$
$= 4 \times 10^{-8}\,\text{mbar L}$
(negligible compared to the amount in-leaking)
With leakage $= 2 \times 10^{-6}$ mbar L s^{-1} entering the component, after 1 h the amount of gas present in the system

$$= 2 \times 10^{-5}\,\text{mbar L s}^{-1} \times 3600\,\text{s}$$
$$= 7.2 \times 10^{-2}\,\text{mbar L}$$

In $40\,\text{cm}^3$ (0.04 L) this would give a pressure of:

$$\frac{7.2 \times 10^{-2}\,\text{mbar L}}{0.04\,\text{L}}$$
$$\underline{= 1.8\,\text{mbar}}$$

(b) On isolation from the pump, the amount of gas present in the system

$$= 1 \times 10^{-6}\,\text{mbar} \times 100\,\text{L}$$
$$= 10^{-4}\,\text{mbar L}$$

(negligible compared to the amount in the component)
On opening the valve to the component, 7.2×10^{-2} mbar L enters the system.

From:
$$p_{\text{comp}} \times V_{\text{comp}} = p_{\text{comp + syst}} \times V_{\text{comp + syst}}$$
$$= p_{\text{comp + syst}} \times (100.00 + 0.04\,\text{L})$$
$$\therefore \quad p_{\text{comp + syst}} = \frac{7.2 \times 10^{-2}\,\text{mbar L}}{100.04\,\text{L}}$$
$$\underline{= 7.2 \times 10^{-4}\,\text{mbar}}$$

A very convenient way of detecting and measuring leaks is to use a tracer gas (such as He) and a selective tracer gas detector, such as a helium leak detector. In addition to the mass spectrometer, MSLD include a high vacuum pumping system of definite pumping speed.

With vacuum systems, the accepted method ('vacuum' method) of leak detection/measurement is to evacuate the object/system under test and with the MSLD coupled *via* its inlet port, apply He externally and observe the response from the MSLD.

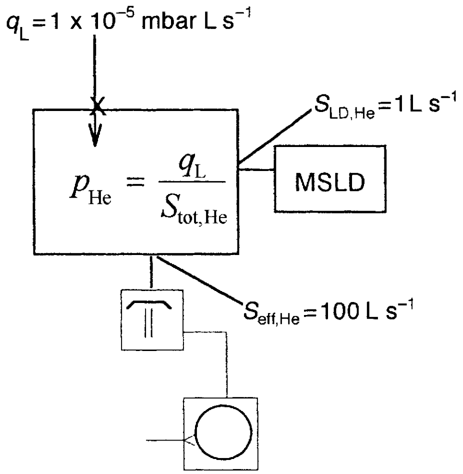
There are two procedures:

(i) for leak localisation – the test object is sprayed methodically on the outside with He. This finds leaks, but total leakage cannot be measured.
(ii) for evaluation of total leakage – the test object is connected to the leak detector and a definite concentration of He is applied to the outside by surrounding it with an enclosure (usually a plastic bag) which is purged before admitting helium.

With MSLDs, it is usually necessary to establish a low pressure (0.1 to a few mbar) at the inlet before quantitative leakage measurements can be made. The pumps in MSLDs used to establish high vacuum conditions in the ion source are frequently used to provide some pumping capacity (usually quite low ($\sim 1\,\mathrm{L\,s^{-1}}$)) at the LD inlet. With small test objects (for example components with volumes < 1 L), evacuation to the test pressure in a reasonable time may be possible just by connecting the leak detector inlet directly to the object. In most cases, however, the size of the system is such that auxiliary vacuum pumps with larger capacity than those in the LD have to be used at the same time. This reduces the sensitivity of the leak test. For testing vacuum systems, either new equipment or as a maintenance and/or fault-finding procedure, the MSLD may be connected either directly to the chamber or to some appropriate point in the pumping set of the system.

Example 4.10

A portable helium leak detector has a pumping speed for He of $1\,\mathrm{L\,s^{-1}}$ at its inlet. It is connected directly to a chamber which has its own pumping system. To reduce the test time and also maintain a low enough pressure for the connection of the leak detector, the chamber's pumping system ($S_{\mathrm{eff,\,He}} = 100\,\mathrm{L\,s^{-1}}$) is used in the test. If the chamber has a leak equivalent to $10^{-5}\,\mathrm{mbar\,L\,s^{-1}}$ He, calculate approximately the leak rate (q_{ind}) which would be shown on the MSLD.



A leak detector shows a signal proportional to the incoming flow of tracer gas.

$$\text{Total flow in system } (q_L) = p_{He}\, S_{eff,He} + p_{He}\, S_{LD,He}$$

$$\therefore \quad \text{Flow to leak detector } = p_{He}\, S_{LD}$$

$$\therefore \quad \frac{\text{Flow to leak detector}}{\text{Total flow } (q_L)} = \frac{p_{He}\, S_{LD}}{p_{He}\, S_{eff} + p_{He}\, S_{LD}}$$

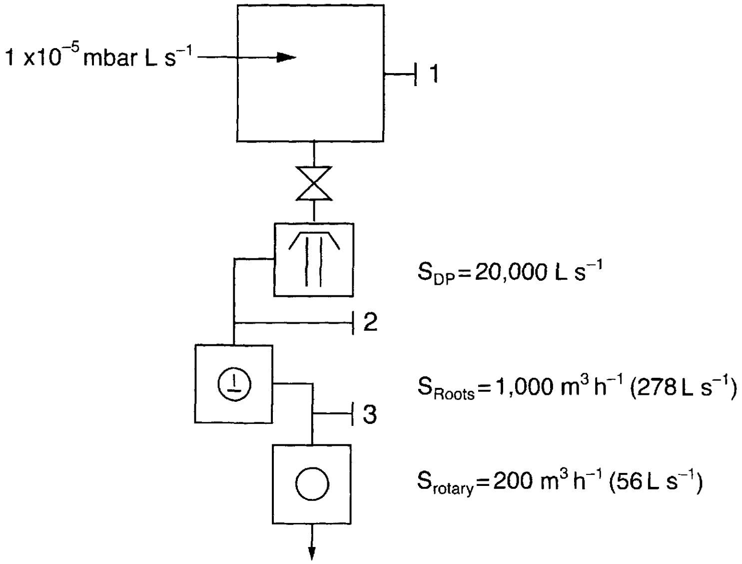
$$\therefore \quad q_{ind} = q_L \frac{S_{LD}}{S_{eff} + S_{LD}} \tag{4.5}$$

$$= 1 \times 10^{-5} \,\text{mbar L s}^{-1} \times \frac{1\,\text{L s}^{-1}}{100\,\text{L s}^{-1} + 1\,\text{L s}^{-1}}$$

$$\underline{\cong 10^{-7}\,\text{mbar L s}^{-1}}$$

Example 4.11

The high vacuum system shown below has a leak of 1×10^{-5} mbar L s^{-1}. It has various ports (shown as 1, 2 and 3 in the diagram) where a leak detector can be connected.



The leak detector has the following characteristics:

- lowest detectable He leak rate = 1×10^{-10} mbar L s^{-1}
- maximum allowable inlet pressure = 0.5 mbar
- pumping speed at inlet = 1 L s^{-1}
- maximum throughput = 10^{-1} mbar L s^{-1}

Assess the effect on its sensitivity of attaching the LD at the various possible positions. Assume that the effective pumping speeds are the given pumping speeds and independent of gas type.

Position 1 Direct connection to the chamber.
From Equation (4.5):

$$q_{\text{ind}} = 1 \times 10^{-5}\,\text{mbar L s}^{-1} \times \frac{1\,\text{L s}^{-1}}{2 \times 10^{4}\,\text{L s}^{-1} + 1\,\text{L s}^{-1}}$$

$$\underline{= 5 \times 10^{-10}\,\text{mbar L s}^{-1}}$$

This is not normally the most effective connection point because the sensitivity is reduced enormously ($S_{\text{DP}} \gg S_{\text{LD}}$) and in this case the indicated leakage is close to the lowest detectable leak rate.

Position 2 Connection between the DP and the backing pump.
In this case the Roots pump is part of the backing pump set.

$$q_{ind} = 1 \times 10^{-5}\,\text{mbar L s}^{-1} \times \frac{1\,\text{L s}^{-1}}{278\,\text{L s}^{-1} + 1\,\text{L s}^{-1}}$$

since $1000\,\text{m}^3\,\text{h}^{-1} = 278\,\text{L s}^{-1}$

$$\underline{q_{ind} = 3.6 \times 10^{-8}\,\text{mbar L s}^{-1}}$$

Position 3 Connection between the outlet of the Roots pump and the inlet to the rotary pump. Here, two situations may arise:

(1) the pressure at the connection point is below 0.5 mbar. In this case:

$$\begin{aligned} q_{\text{ind}} &= 1 \times 10^{-5}\,\text{mbar L s}^{-1} \times \frac{1\,\text{L s}^{-1}}{56\,\text{L s}^{-1} + 1\,\text{L s}^{-1}} \\ &\underline{= 1.8 \times 10^{-7}\,\text{mbar L s}^{-1}} \end{aligned}$$

(2) the pressure at the connection point is above 0.5 mbar. In this case a throttle must be inserted between the system and the MSLD. The throttle can then be adjusted to give the maximum throughput acceptable to the MSLD (10^{-1} mbar L s^{-1}). The indicated leak will then depend on the amount of gas handled by the DP. For example, it is not unexpected for a 20 000 L s^{-1} diffusion pump operating at 10^{-2} mbar to have $S_{\text{DP}} \sim 1800\,\text{L s}^{-1}$ (see Figure 3.9 and Example 3.11). Therefore $q_{pV} = 18\,\text{mbar L s}^{-1}$.

$$\frac{q_{\text{ind}}}{q_{\text{L}}} = \frac{q_{\text{pV,MSLD,max}}}{q_{\text{pV,DP}}}$$

So,

$$\begin{aligned} q_{\text{ind}} &= 1 \times 10^{-5}\,\text{mbar L s}^{-1} \times \frac{10^{-1}\,\text{mbar L s}^{-1}}{18\,\text{mbar L s}^{-1}} \\ &\underline{= 5.6 \times 10^{-8}\,\text{mbar L s}^{-1}} \end{aligned}$$

In leak detection, as rapid a response as possible is required from the test object–leak detector arrangement. It is generally assumed that the signal from the leak detector in the presence of He builds up exponentially (and decays in a similar manner after He investigation stops). In such a case, the response time (t) is expressed in terms of a time constant (τ). For an increase in signal to 63% of its equilibrium value:

$$t_{63\%} = \tau = \frac{V}{S} \tag{4.6}$$

where V is the internal volume of the test object and S is the pumping speed for He of the arrangement.

For 95% of the steady-state signal:

$$t_{95\%} = 3\tau = 3\frac{V}{S} \tag{4.7}$$

For the steady-state signal:

$$t_{\mathrm{SS}} = 5\tau = 5\frac{V}{S} \tag{4.8}$$

Example 4.12

The chamber in Example 4.11 has a volume of 5 m^3. The volumes of the diffusion pump and the connecting line to the chamber are 100 L and 660 L, respectively. The volume of the connection between the Roots and diffusion pumps is 10 L. Calculate the response time for 95% of the final signal on the leak detector when it is connected in positions 1 and 2.

From Equation (4.7) the response time to 95% signal ($t_{95\%}$) is $3\frac{V}{S}$.

In position (1):

$$\begin{aligned} t_{95\%} &= 3\frac{V}{S} = \frac{3 \times (5000\,\mathrm{L} + 660\,\mathrm{L})}{(2 \times 10^4\,\mathrm{L\,s^{-1}} + 1\,\mathrm{L\,s^{-1}})} \\ &= \underline{0.9\,\mathrm{s}} \end{aligned}$$

In position (2), the response time would include the above time and the additional time:

$$\begin{aligned} t_{95\%} &= 0.9\,\mathrm{s} + \frac{3\,(100\,\mathrm{L} + 10\,\mathrm{L})}{(278\,\mathrm{L\,s^{-1}} + 1\,\mathrm{L\,s^{-1}})} \\ &= 0.9\,\mathrm{s} + 1.2\,\mathrm{s} \\ &= \underline{2.1\,\mathrm{s}} \end{aligned}$$

4.3 OUTGASSING

Any material which has been exposed to – or manufactured in – atmospheric air will have gas adsorbed on the surface, or dissolved or absorbed in the bulk. On evacuation, therefore, the walls of a vacuum system and the components and material being processed inside will tend to re-emit this gas. This phenomenon is generally termed outgassing.

It is not possible to predict outgassing behaviour from even a detailed knowledge of surface composition, and so a considerable number of measurements have been made on the range of materials likely to be used in the fabrication of vacuum systems or to be processed within them. Outgassing from a surface decreases with pumping time. A relatively simple formula can be used to describe measured data.

At constant temperature, the time-dependence of outgassing follows the relationship:

$$\dot{q}_{\text{outg}} = \frac{a_{1\,\text{h}}\,A}{(t/1\,\text{h})^{\alpha}} \tag{4.9}$$

where $\dot{q}_{\text{outg}}$ is the throughput due to outgassing
A is the geometrical surface area
a_{1h} is a fit parameter identified as the specific outgassing rate after 1 h
α is the exponent of decay. It is the negative slope of the outgassing curve presented as a log/log plot of $\dot{q}/A$ *vs* time

For metals, ceramics and glasses, this formula is applicable for times up to 100 h or more. With polymers (*e.g.* PTFE, Nylon, *etc.*), a single set of parameters for Equation (4.9) may be insufficient to fit the observed behaviour over a given time interval and the further use of Equation (4.9) with other parameters may be necessary. Values of α cover a range from 0.2 to 1.2 but $\alpha = 1$ or 0.5 are frequently found. The former value is shown for metals, glasses and ceramics and indicates desorption predominantly from the surface of the material. The value of 0.5 is associated with plastics and elastomers and indicates diffusion-controlled outgassing from the bulk.

Polymeric materials generally show higher outgassing rates than metals and ceramics. At room temperature it is accepted that, for materials previously exposed to ambient air, 80% or more of the outgassing flow is water vapour. Apart from water, however, some polymers release volatile organic compounds.

For a vacuum system made of and/or containing various materials, the overall outgassing flow is the sum of the contributions from all the materials. Thus:

$$\dot{q}_{\text{tot,outg}} = \frac{a_{1\text{h},1}\,A_1}{(t/1\text{h})^{\alpha_1}} + \frac{a_{1\text{h},2}A_2}{(t/1\text{h})^{\alpha_2}} + \frac{a_{1\text{h},3}\,A_3}{(t/1\text{h})^{\alpha_3}} + \ldots \tag{4.10}$$

where $a_{1\text{h},1}$ and α_1 are the fit parameters for material 1, $a_{1\text{h},2}$ and α_2 are the fit parameters for material 2 and so on.

Some values of a_{1h} and α are given in Table 4.1

Table 4.1 *Some outgassing parameters for various materials*

Material	a_{1h} (mbar L s^{-1} cm^{-2})	α
Stainless steel		
baked $T > 120\,°C$	5×10^{-9}	1
electropolished	5×10^{-8}	1
no special treatment	3×10^{-7}	1
Al and Al-Mg alloys	6×10^{-9}	1
Mild steel	5×10^{-7}	1
PTFE	6×10^{-7}	0.6
PVC		
hard	1×10^{-6}	0.5
soft	1×10^{-3}	0.5

Example 4.13

The walls of a vacuum system have a surface area of $4\,\mathrm{m}^2$. The specific outgassing rate (a_{1h}) is $4 \times 10^{-4}\,\mathrm{Pa\,m^3\,s^{-1}\,m^{-2}}$ and $\alpha = 1$. If it is assumed that there are no other significant gas sources, calculate the pumping speed necessary to achieve 10^{-4} mbar after 55 min.

From Equation (4.9):

$$\dot{q}_{\mathrm{outg,55min}} = \frac{4 \times 10^{-4}\,\mathrm{Pa\,m^3\,s^{-1}\,m^{-2}} \times 4\,\mathrm{m^2}}{(55/60)^1}$$

$$= 1.75 \times 10^{-3}\,\mathrm{Pa\,m^3\,s^{-1}}$$

$$= 17.5 \times 10^{-3}\,\mathrm{mbar\,L\,s^{-1}}$$

If $p = 10^{-4}\,\mathrm{mbar}$

then

$$S = \frac{\dot{q}_{\mathrm{outg}}}{p}$$

$$= \frac{17.5 \times 10^{-3}\,\mathrm{mbar\,L\,s^{-1}}}{10^{-4}\,\mathrm{mbar}}$$

$$= \underline{175\,\mathrm{L\,s^{-1}}}$$

Example 4.14

A typical outgassing rate for austenitic stainless steel is $9 \times 10^{-8}\,\mathrm{mbar\,L\,s^{-1}\,cm^{-2}}$ after 1 h pumping at room temperature. What would be the outgassing load in a chamber made of the same material having a surface area of $0.9\,\mathrm{m}^2$, after 3 h pumping?

$$a_1 = 9 \times 10^{-8}\,\text{mbar L s}^{-1}\,\text{cm}^{-2};\ \text{assume } \alpha = 1$$

$$\begin{aligned}\dot{q}_{\text{outg,3h}} &= \frac{9 \times 10^{-8}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 9000\,\text{cm}^2}{(3/1)^1} \\ &= 3 \times 10^{-8} \times 9 \times 10^3\,\text{mbar L s}^{-1} \\ &= \underline{2.7 \times 10^{-4}\,\text{mbar L s}^{-1}}\end{aligned}$$

Example 4.15

A sample of an aluminium alloy to be used in the manufacture of a UHV system has a degassing rate of $5 \times 10^{-10}\,\text{mbar L s}^{-1}\,\text{cm}^{-2}$ after pumping for 10 h.

(a) Estimate the value of the specific outgassing constant.
(b) Calculate the amount of outgassing after 6 h for a spherical chamber having a volume of 56 L.

(a)

$$\dot{q}_{\text{outg}} = \frac{a_{1\text{h}} A}{(t/1\,\text{h})^{\alpha}}$$

if $\alpha = 1$ then, for $A = 1\,\text{cm}^2$

$$\begin{aligned}a_{1\text{h}} &= q_{\text{outg,10h}} \times 10 \\ &= \underline{5 \times 10^{-9}\,\text{mbar L s}^{-1}\,\text{cm}^{-2}}\end{aligned}$$

(b) Volume of spherical chamber $= 56\,000\,\text{cm}^3$

$$= \frac{4\pi r^3}{3}$$

$$\therefore\quad r = 23.7\,\text{cm}$$

Area of chamber $= 4\pi r^2$
$= 7058\,\text{cm}^2$

$$\therefore\quad \dot{q}_{\text{outg}} = a_{1\text{h}} \times \frac{7058}{6}$$

$$\begin{aligned}&= 5 \times 10^{-9}\,\text{mbar L s}^{-1}\text{cm}^{-2} \times \frac{7058\,\text{cm}^2}{6} \\ &\cong \underline{5.9 \times 10^{-6}\,\text{mbar L s}^{-1}}\end{aligned}$$

Example 4.16

A vacuum system, made of stainless steel, has an internal surface area of $3\,\text{m}^2$. In the chamber, there are several electrical connections insulated with PTFE. The polymer surface area is $0.3\,\text{m}^2$. If the outgassing constants $a_{1\text{h}}$ and α are $3 \times 10^{-7}\,\text{mbar L s}^{-1}\,\text{cm}^{-2}$ and 1, respectively, for stainless steel and 6×10^{-7} mbar L s^{-1} cm^{-2} and 0.6 for PTFE, calculate the total outgassing flow rate ($\dot{q}_{outg}$) for the system after (a) 1 hour (b) 3 hours (c) 6 hours pumping.

(a)
$$\dot{q}_{outg,ss,1h} = \frac{3 \times 10^{-7}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 3 \times 10^{4}\,\text{cm}^{2}}{(1/1)^{1}} = 9 \times 10^{-3}\,\text{mbar L s}^{-1}$$

$$\dot{q}_{outg,PTFE,1h} = \frac{6 \times 10^{-7}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 3 \times 10^{3}\,\text{cm}^{2}}{(1/1)^{0.6}} = 1.8 \times 10^{-3}\,\text{mbar L s}^{-1}$$

$$\therefore \quad \dot{q}_{outg,tot} = \underline{10.8 \times 10^{-3}\,\text{mbar L s}^{-1}}$$

(b)
$$\dot{q}_{outg,ss,3h} = \frac{3 \times 10^{-7}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 3 \times 10^{4}\,\text{cm}^{2}}{(3)} = 3 \times 10^{-3}\,\text{mbar L s}^{-1}$$

$$\dot{q}_{outg,PTFE,3h} = \frac{6 \times 10^{-7}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 3 \times 10^{3}\,\text{cm}^{2}}{(3)^{0.6}}$$

$$= \frac{18 \times 10^{-4}\,\text{mbar L s}^{-1}}{1.933} = 9.3 \times 10^{-4}\,\text{mbar L s}^{-1}$$

$$\therefore \quad \dot{q}_{outg,tot} = \underline{3.93 \times 10^{-3}\,\text{mbar L s}^{-1}}$$

(c)
$$\dot{q}_{outg,ss,6h} = \frac{3 \times 10^{-7}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 3 \times 10^{4}\,\text{cm}^{2}}{(6)} = 1.5 \times 10^{-3}\,\text{mbar L s}^{-1}$$

$$\dot{q}_{outg,PTFE,6h} = \frac{6 \times 10^{-7}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 3 \times 10^{3}\,\text{cm}^{2}}{(6)^{0.6}}$$

$$= \frac{18 \times 10^{-4}\,\text{mbar L s}^{-1}}{(6)^{0.6}} = 6.1 \times 10^{-4}\,\text{mbar L s}^{-1}$$

$$\therefore \quad \dot{q}_{outg,tot} = \underline{2.11 \times 10^{-3}\,\text{mbar L s}^{-1}}$$

Example 4.17

From the data calculated in Example 4.16, estimate what proportion of the total gas load after 1, 3 and 6 h is evolved from the PTFE. Comment on the result.

$$\text{PTFE contribution to total after 1 h,} \quad = \frac{1.8 \times 10^{-3}}{10.8 \times 10^{-3}} = 17\%$$

$$\text{after 3 h} \quad = \frac{0.93 \times 10^{-3}}{3.93 \times 10^{-3}} = 24\%$$

$$\text{after 6 h} \quad = \frac{0.61 \times 10^{-3}}{2.11 \times 10^{-3}} = 29\%$$

This indicates that, with time, gas evolution from PTFE (mostly water vapour) becomes an increasingly important gas source. This behaviour is typical of polymers and elastomers.

Example 4.18

A laboratory system is pumped by a turbomolecular pump ($S_{\text{eff}} = 600\,\text{L s}^{-1}$) to 6×10^{-6} mbar in 30 min.

(a) What will be the pressure and pV throughput after 1 h pumping if the outgassing exponent (α) = 1 and other gas sources are negligible?

(b) What pressure will be reached after 12 h?

At 6×10^{-6} mbar, $\dot{q}_{pV}$ to the pump is given by:

$$\begin{aligned}\dot{q}_{pV} = p \times S_{\text{eff}} &= 6 \times 10^{-6}\,\text{mbar} \times 600\,\text{L s}^{-1}\\ &= 3.6 \times 10^{-3}\,\text{mbar L s}^{-1}\end{aligned}$$

(a) If $\dot{q}_{pV}$ (above) is due to outgassing then, from Equation (4.9):

$$3.6 \times 10^{-3}\,\text{mbar L s}^{-1} = \frac{a_{1\text{h}}A}{(30/60)^1}$$

$$\therefore \quad a_{1\text{h}}A = 1.8 \times 10^{-3}\,\text{mbar L s}^{-1}$$

After 1 h: $$\dot{q}_{pV} = 1.8 \times 10^{-3}\,\text{mbar L s}^{-1}$$

and $$p = \frac{1.8 \times 10^{-3}\,\text{mbar L s}^{-1}}{600\,\text{L s}^{-1}}$$

$$= 3 \times 10^{-6}\,\text{mbar}$$

(b) After 12 h: $$\dot{q}_{pV} = \frac{1.8 \times 10^{-3}}{(12/1)^1}\,\text{mbar L s}^{-1}$$

$$= 1.5 \times 10^{-4}\,\text{mbar L s}^{-1}$$

and $$p = \frac{1.5 \times 10^{-4}\,\text{mbar. L s}^{-1}}{600\,\text{L s}^{-1}}$$

$$= \underline{2.5 \times 10^{-7}\,\text{mbar}}$$

4.4 PERMEATION

All materials show some permeability to gases. In vacuum applications, gas transmission involves three stages:

(i) adsorption of gas on the high-pressure side
(ii) diffusion through the material
(iii) desorption of gas on the low-pressure side.

The process is strongly temperature dependent although, even at high temperatures, the metals and alloys used in the fabrication of vacuum systems can be regarded as impermeable to air. The highest permeability for a gas through metals is usually observed with H_2, *e.g.* H_2 permeates significantly through Pd.

The permeation of air through some elastomers can be significant and is shown in Figure 4.2.

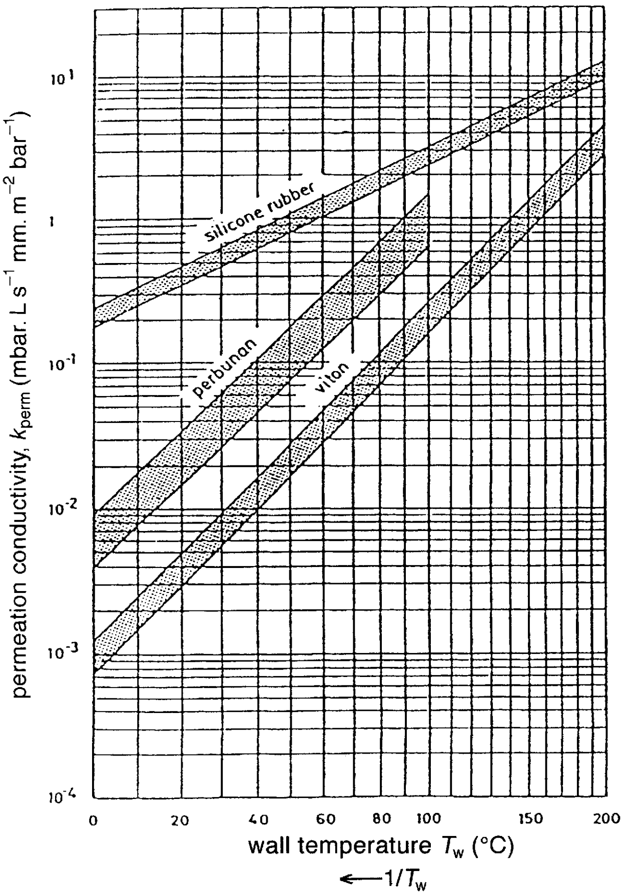


Figure 4.2 *Permeation conductivity for some elastomers in the presence of air*

(Reproduced from ref. (d′), p. 509 with permission of Fr. Vieweg & Sohn Verlagsgellschaft mbH, Wiesbaden)

At constant temperature and for gases such as O_2, N_2 and H_2O which permeate as molecules, the permeability of a material can be expressed as a permeation flow rate ($\dot{q}_{pV,\text{perm}}$):

$$\dot{q}_{pV,\text{perm}} = k_{\text{perm}} \frac{A}{d}(p_1 - p_2) \tag{4.11}$$

where A is the cross-sectional area through which permeation takes place, k_{perm} is the permeation conductivity (by analogy to thermal conductivity (Adam in (ref. (d), p. 506)), d is the thickness and p_1, p_2 are the high pressure and low pressure values, respectively.

If k_{perm} is in units of mbar L s^{-1} mm m^{-2} bar^{-1}, A in m^2, d in mm and p in bar, then $\dot{q}_{\text{perm}}$ has units of mbar L s^{-1}.

For a gas such as H_2 that dissociates on adsorption, Equation (4.11) must be modified so that:

$$\dot{q}_{pV,\text{perm}} = k_{\text{perm}} \frac{A}{d}\left(p_1^{\frac{1}{2}} - p_2^{\frac{1}{2}}\right) \tag{4.11a}$$

Example 4.19

The permeability of borosilicate glass to He is about 3×10^{-6} mbar L s^{-1} mm m^{-2} bar^{-1} at 20 °C. Its permeability is due to its quartz content, quartz having a high permeability to He. A system is fitted with 5 × DN100CF observation windows made of borosilicate glass (thickness = 6 mm).

(a) Calculate the permeation throughput of air (containing 5 ppm He) into the system *via* the windows if the system is evacuated to negligibly low pressure.
(b) During prolonged leak checking in which excessive He was used, the concentration of He in air close to the windows increased to 10^3 ppm. Calculate the He throughput into the system.

Ignore leaks in both cases.

(a) From Equation (4.11):

$$\dot{q}_{pV,\text{perm}} = \frac{3 \times 10^{-6}\,\text{mbar L s}^{-1}\,\text{mm m}^{-2}\,\text{bar} \times A\,\text{m}^2 \times 5 \times 10^{-6}\,\text{bar}}{6\,\text{mm}}$$

$$A_{\text{window}} = \frac{5 \times \pi \times 10.2^2\,\text{cm}^2}{4} = 409\,\text{cm}^2 = 0.041\,\text{m}^2$$

$$\therefore \quad \dot{q}_{pV,\mathrm{perm}} = \frac{3 \times 10^{-6} \times 0.041\,\mathrm{m}^2 \times 5 \times 10^{-6}}{6}\,\mathrm{mbar\,L\,s^{-1}}$$

$$= \underline{1 \times 10^{-13}\,\mathrm{mbar\,L\,s^{-1}}\ \text{(negligible)}}$$

(b) From Equation (4.11):

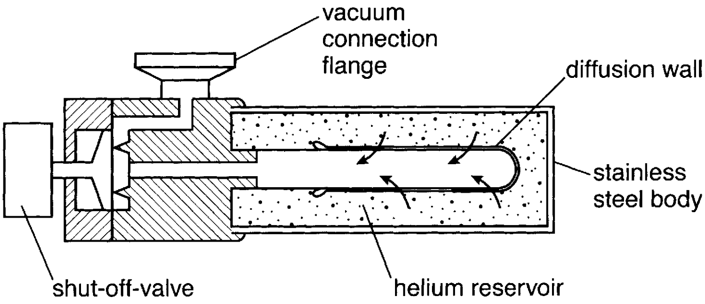
$$\dot{q}_{pV,\mathrm{perm}} = \frac{3 \times 10^{-6}\,\mathrm{mbar\,L\,s^{-1}\,mm\,m^{-2}\,bar} \times 0.041\,\mathrm{m}^2 \times 10^{-3}\,\mathrm{bar}}{6\,\mathrm{mm}}$$

$$= \underline{2.1 \times 10^{-11}\,\mathrm{mbar\,L\,s^{-1}}}$$

The permeation of He through quartz glass is exploited in He leak detection. Test leaks have many applications including the calibration of MSLD (Section 4.3) and the assessment of the sensitivity and response time of the system.

Example 4.20

A test leak (shown below) consists of a quartz diffusion barrier of length 70 mm, internal diameter (d') 10 mm and wall thickness (d) 1 mm. If the reservoir contains 400 mbar He and discharges into a vacuum *via* the vacuum connection flange, calculate the leakage at 20 °C (k_{perm} quartz glass = 5×10^{-5} mbar L s^{-1} mm m^{-2} bar).



Surface area of quartz glass = $\pi d' l = 22\,\mathrm{cm}^2$; $d = 1$ mm

$$\therefore \quad \dot{q}_{pV,\mathrm{perm}} = 5 \times 10^{-5}\,\mathrm{mbar\,L\,s^{-1}\,mm\,m^{-2}\,bar} \times \frac{22\,\mathrm{m}^2}{10^4} \times \frac{0.4\,\mathrm{bar}}{1\,\mathrm{mm}}$$

$$= \underline{4.4 \times 10^{-8}\,\mathrm{mbar\,L\,s^{-1}}}$$

Example 4.21

A He permeation test leak has a nominal value of 3.5×10^{-8} mbar L s^{-1} at 23 °C. It has a reservoir (200 cm^3) filled with He at 400 mbar. How long will it take before the leakage has fallen by 10%?

$$\dot{q}_{pV,\text{perm}} \text{ at } t = 0 = 3.5 \times 10^{-8}\,\text{mbar L s}^{-1}$$
$$\dot{q}_{pV,\text{perm}} \text{ at } t = t = 3.15 \times 10^{-8}\,\text{mbar L s}^{-1}$$

In this time, the reservoir pressure has fallen from 0.4 bar to 0.36 bar.

Assuming that loss of He can be modelled as a pumping process, then:

$$\dot{q}_{pV,t=0} = 3.5 \times 10^{-8}\,\text{mbar L s}^{-1} = p_{t=0} \times S_{\text{eff}} = 400\, S_{\text{eff}}\,\text{mbar L s}^{-1}$$

$$\text{then } S_{\text{eff}} = \frac{3.5 \times 10^{-8}}{400}\,\text{L s}^{-1}$$
$$= \underline{8.75 \times 10^{-11}\,\text{L s}^{-1}}$$

The time taken for the pressure in the reservoir to fall from 0.4 to 0.36 bar can be calculated from the standard expression:

$$t = \frac{V}{S_{\text{eff}}}\, ln \frac{p_{t=0}}{p_{t=t}}$$

$$\therefore \quad t = \frac{0.2\,\text{L}}{8.75 \times 10^{-11}\,\text{L s}^{-1}} \times 2.303 \log \frac{400}{360}$$
$$= \frac{0.2 \times 2.303 \times 0.0458}{8.75 \times 10^{-11}}\,\text{s}$$
$$= 2.41 \times 10^{-3} \times 10^{11}\,\text{s}$$
$$= 2.41 \times 10^{8}\,\text{s}$$
$$= \underline{7.6 \text{ years}}$$

Example 4.22

According to Figure 4.2, k_{perm} for air for an FPM elastomer (*e.g.* Viton) at 30 °C is (7.5 ± 2) × 10^{-3} mbar L s^{-1} mm m^{-2} bar. For a DN250 component attached to a vacuum system by an O-ring (normal diameter = 5 mm; in compressed state, assume an elliptical cross-section of height (*h*) 2.5 mm and width (*d*) 8 mm), calculate the permeation flow rate through the O-ring.

$$\dot{q}_{pV,\text{perm}} = k_{\text{perm}} \frac{A}{d} \Delta p$$

$$= (7.5 \pm 2) \times 10^{-3}\,\text{mbar L s}^{-1}\,\text{mm m}^{-2}\,\text{bar} \times \pi d'_{\text{O-ring}} \times h_{\text{O-ring}} \times \frac{1}{8}\,\text{mm}^{-1} \times 1\,\text{bar}$$

$$= (7.5 \pm 2) \times 10^{-3}\,\text{mbar L s}^{-1}\,\text{mm m}^{-2}\,\text{bar} \times \frac{82 \times 0.25}{10^4}\,\text{m}^2 \times \frac{1}{8}\,\text{mm}^{-1} \times 1\,\text{bar}$$

$$\underline{= (1.9 \pm 0.5) \times 10^{-6}\,\text{mbar L s}^{-1}}$$

Note: $d'_{\text{DN250}} = 261$ mm so $\pi d' = 82$ cm.

Example 4.23

A cylindrical vacuum chamber ($d = 0.75$ m, $l = 3$ m) has demountable ends sealed with O-rings (uncompressed diameter of O-ring material = 5 mm; dimensions in the compressed state as in Example 4.22). The chamber is fitted with 10 × DN40 KF O-ring sealed feedthroughs (diameter of O-ring material in the uncompressed state = 3 mm; on compression O-ring material assumes an elliptical cross-section with height 2 mm and width 4 mm). All O-rings are made of NBR elastomer *e.g.* Perbunan.

(a) Calculate the flow rate due to permeation into the evacuated chamber at 25 °C.
(b) If the chamber is made of stainless steel ($a_{1\text{h}} = 5 \times 10^{-8}\,\text{mbar L s}^{-1}\,\text{cm}^{-2}$), compare the total gas load after 24 h and 48 h pumping with the throughput due to permeation.

(a) For NBR elastomers, from Figure 4.2, $k = 3 \times 10^{-2}\,\text{mbar L s}^{-1}\,\text{mm m}^{-2}\,\text{bar}$ at 25 °C.

For the door seals:

$$\text{total permeating length} = \pi d \times 2$$
$$= 4.72\,\text{m}$$

$$\text{permeating area} = 4.72 \times \frac{2.5}{10^3}\,\text{m}^2$$
$$= 0.012\,\text{m}^2$$

$$\therefore \quad \dot{q}_{pV,\text{perm,doors}} = 3 \times 10^{-2}\,\text{mbar L s}^{-1}\,\text{mm m}^{-2}\,\text{bar} \times 0.012\,\text{m}^2 \times \frac{1}{8}\,\text{mm}^{-1} \times 1\,\text{bar}$$
$$\underline{= 4.4 \times 10^{-5}\,\text{mbar L s}^{-1}}$$

For 10 × DN40 KF O-rings:

$$\text{total permeating length} = \pi d \times 10$$
$$= 1.29\,\text{m}$$

$$\text{permeating area} \quad = 1.29\,\text{m} \times \frac{2}{10^3}\,\text{m}$$

$$= 2.6 \times 10^{-3}\,\text{m}^2$$

$$\therefore \quad \dot{q}_{pV,\text{perm,DN40}} = 3 \times 10^{-2}\,\text{mbar L s}^{-1}\,\text{mm m}^{-2}\,\text{bar} \times 2.6 \times 10^{-3}\,\text{m}^2 \times \frac{1}{4}\,\text{mm}^{-1} \times 1\,\text{bar}$$

$$\underline{= 1.95 \times 10^{-5}\,\text{mbar L s}^{-1}}$$

$$\therefore \quad \dot{q}_{pV,\text{perm,total}} = \underline{6.4 \times 10^{-5}\,\text{mbar L s}^{-1}}$$

(b)

$$\dot{q}_{\text{outg}} = \frac{a_1 A}{(t/1\,\text{h})^{\alpha}}$$

$$A = \pi d \times l + 2\pi \frac{d^2}{4}$$

$$\cong 8 \times 10^4\,\text{cm}^2$$

$$\therefore \quad \dot{q}_{\text{outg,24h}} = \frac{5 \times 10^{-8}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 8 \times 10^4\,\text{cm}^2}{24}$$

$$= \frac{4 \times 10^{-3}}{24}\,\text{mbar L s}^{-1}$$

$$\underline{\cong 1.7 \times 10^{-4}\,\text{mbar L s}^{-1}}$$

Although permeation is significant, it is only 27% of the gas load into the system, even after 24h pumping.

$$\therefore \quad \dot{q}_{\text{outg,48h}} = \frac{a_1 A}{(\text{t}/1\,\text{h})^{\alpha}}$$

$$= \frac{5 \times 10^{-8}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 8 \times 10^4\,\text{cm}^2}{48}$$

$$\underline{= 8.3 \times 10^{-5}\,\text{mbar L s}^{-1}}$$

After 48 h, permeation is contributing 43% to the gas load in the system.

4.5 ATTAINABLE PRESSURE

The required vacuum pressure in a system can only be achieved if the vacuum pump can deal with the gas load. Low gas pressures can be obtained if:

(i) $q_{pV,\text{leakage}}$ and $q_{pV,\text{perm}}$ are sufficiently low and
(ii) $q_{pV,\text{outg}}$ is small enough and
(iii) $q_{pV,\text{pump backstreaming}}$ is negligible.

Example 4.24

A cylindrical vacuum chamber has an internal diameter of 70 cm and a length of 2.5 m. It is made of cleaned stainless steel and evacuated with a combination of diffusion and rotary vacuum pumps. Measurements of the outgassing rate of the chamber material, cleaned according to the same method, give the following data:

time (s)	outgassing rate (Pa m^3 s^{-1} m^{-2})
10^3	1.9×10^{-3}
10^4	1.9×10^{-4}
10^5	1.9×10^{-5}

(a) What is the rate of gas flow from the walls after 45 minutes of pumping?
(b) If the chamber has a leakage rate of 6×10^{-3} mbar L s^{-1}, what is the effective pumping speed of the diffusion pump if a pressure of 1×10^{-5} mbar is to be achieved after 45 min?
(c) What is the achievable base pressure for the system?

(a) After 10^3 s, the outgassing rate from the walls is 1.9×10^{-3} Pa m^3 s^{-1} m^{-2}:

$$\therefore \quad a_1 = 5.28 \times 10^{-4}\ \text{Pa m}^3\,\text{s}^{-1}\,\text{m}^{-2}$$

(check by calculating $q_{\text{out},10^4\text{s}}$ and $q_{\text{out},10^5\text{s}}$).
Assuming that the chamber ends are hemispherical, the area of the walls and chamber ends (neglecting the entrance area of the diffusion pump, gauges, *etc.*) is:

$$A_{\text{tot}} = A_{\text{walls}} + A_{\text{ends}} = \pi d l + \frac{4\pi r^2}{2} \times 2$$

where d and r are the chamber diameter and radius, respectively, and l is the chamber length.

$$\begin{aligned} &= 5.5\ \text{m}^2 + 1.54\ \text{m}^2 \\ &= 7.04\ \text{m}^2 \end{aligned}$$

$$\therefore \quad \dot{q}_{\text{outg,45min}} = \frac{5.28 \times 10^{-4}\ \text{Pa m}^3\,\text{s}^{-1}\,\text{m}^{-2} \times 7.04\ \text{m}^2}{(45/60)^1}$$

$$\begin{aligned} &= 5.0 \times 10^{-3}\ \text{Pa m}^3\,\text{s}^{-1} \\ &= \underline{5.0 \times 10^{-2}\ \text{mbar L s}^{-1}} \end{aligned}$$

(b)

$$\begin{aligned}\dot{q}_{\text{tot,45min}} &= \dot{q}_{\text{leak}} + \dot{q}_{\text{outg}} \\ &= 0.6 \times 10^{-2}\,\text{mbar L s}^{-1} + 5.0 \times 10^{-2}\,\text{mbar L s}^{-1} \\ &= 5.6 \times 10^{-2}\,\text{mbar L s}^{-1}\end{aligned}$$

From:

$$p = \frac{\dot{q}_{\text{tot}}}{S_{\text{eff}}}$$

$$\begin{aligned}S_{\text{eff}} &= \frac{\dot{q}_{\text{tot}}}{p} \\ &= \frac{5.6 \times 10^{-2}\,\text{mbar L s}^{-1}}{1 \times 10^{-5}\,\text{mbar}} \\ &= \underline{5600\,\text{L s}^{-1}}\end{aligned}$$

(c) The base pressure of the system will ultimately be determined by leakage into the chamber

$$\begin{aligned}\therefore\quad p_{\text{base}} &= \frac{6 \times 10^{-3}\,\text{mbar L s}^{-1}}{5600\,\text{L s}^{-1}} \\ &= \underline{1.1 \times 10^{-6}\,\text{mbar}}\end{aligned}$$

Example 4.25

A vacuum vessel ($V = 50\,\text{L}$) is evacuated by a diffusion pump backed with a two-stage rotary vacuum pump. There is a leakage of air into the vessel and a desorption gas load (water vapour) of $1 \times 10^{-4}\,\text{mbar L s}^{-1}$. The pumping speeds of the diffusion pump for air and water vapour are $100\,\text{L s}^{-1}$ and $120\,\text{L s}^{-1}$, respectively. Between the diffusion pump and the vessel is a valve having a conductance for air of $100\,\text{L s}^{-1}$.

(a) If a pressure of 5×10^{-6} mbar is established in the vessel: (i) How large is the air leak? (ii) What are the partial pressures of air and water vapour? (iii) What would be the total pressure immediately above the diffusion pump (assume that when the valve is fully closed, the pressure above the diffusion pump is negligibly small)?

(b) If the valve is kept closed for 1000 s, what is the pressure in the vessel? (Assume the outgassing flux remains constant with time.)

(a)(i) We need to find the effective pumping speed of the diffusion pump above the valve for air and for water vapour:

$S_{\text{eff,air}}$

From Equation (2.5):

$$\frac{1}{S_{\text{eff,air}}} = \frac{1}{S_{0,\text{air}}} + \frac{1}{C_{\text{valve,air}}} = \frac{1}{100} + \frac{1}{100}$$

$$\therefore \quad S_{\text{eff,air}} = \underline{50\,\text{L s}^{-1}}$$

$S_{\text{eff,H}_2\text{O}}$

From Equation (2.38):

$$C_{\text{valve,H}_2\text{O}} = C_{\text{valve,air}}\sqrt{\frac{M_{\text{air}}}{M_{\text{H}_2\text{O}}}}\,\text{L s}^{-1}$$

$$= 100\sqrt{\frac{29}{18}}\,\text{L s}^{-1}$$

$$= 127\,\text{L s}^{-1}$$

$$\frac{1}{S_{\text{eff,H}_2\text{O}}} = \frac{1}{S_{0,\text{H}_2\text{O}}} + \frac{1}{C_{\text{valve,H}_2\text{O}}} = \frac{1}{120} + \frac{1}{127}$$

$$\therefore \quad S_{\text{eff,H}_2\text{O}} = \underline{61.7\,\text{L s}^{-1}}$$

In the vacuum vessel:

$$p_{\text{tot}} = p_{\text{air}} + p_{\text{H}_2\text{O}} = \frac{q_{pV,\text{air}}}{S_{\text{eff,air}}} + \frac{q_{pV,\text{H}_2\text{O}}}{S_{\text{eff,H}_2\text{O}}}$$

$$\therefore \quad 5 \times 10^{-6}\,\text{mbar} = \frac{q_{pV,\text{air}}}{50\,\text{L s}^{-1}} + \frac{1 \times 10^{-4}\,\text{mbar L s}^{-1}}{61.7\,\text{L s}^{-1}}$$

$$\therefore \quad q_{pV,\text{air}} = \underline{1.7 \times 10^{-4}\,\text{mbar L s}^{-1}}$$

(ii)

$$p_{\text{air}} = \frac{1.7 \times 10^{-4}\,\text{mbar L s}^{-1}}{50\,\text{L s}^{-1}} = 3.4 \times 10^{-6}\,\text{mbar}$$

$$p_{\text{H}_2\text{O}} = \frac{1 \times 10^{-4}\,\text{mbar L s}^{-1}}{61.7\,\text{L s}^{-1}} = 1.6 \times 10^{-6}\,\text{mbar}$$

(iii)

$$p_{\text{tot}} = p_{\text{air}} + p_{\text{H}_2\text{O}}$$

$$= \frac{1.7 \times 10^{-4}\,\text{mbar L s}^{-1}}{100\,\text{L s}^{-1}} + \frac{1 \times 10^{-4}\,\text{mbar L s}^{-1}}{120\,\text{L s}^{-1}}$$

$$= 1.7 \times 10^{-6}\,\text{mbar} + 0.83 \times 10^{-6}\,\text{mbar}$$

$$= \underline{2.5 \times 10^{-6}\,\text{mbar}}$$

(b) If the valve is fully closed for 1000 s, the established base pressure for the system (5×10^{-6} mbar) will change by Δp which is given by:

$$q_{pV,\text{air}} + q_{pV,\text{H}_2\text{O}} = V\frac{\Delta p}{\Delta t}$$

$$\therefore \quad \Delta p = \frac{(q_{pV,\text{air}} + q_{pV,\text{H}_2\text{O}})\,\text{mbar L s}^{-1} \times 1000\,\text{s}}{50\,\text{L}}$$

$$= 5.4 \times 10^{-3}\,\text{mbar}$$

$$p_{\text{vessel}} = 5 \times 10^{-6}\,\text{mbar} + 5.4 \times 10^{-3}\,\text{mbar}$$

$$= \underline{5.4 \times 10^{-3}\,\text{mbar}}$$

Example 4.26

The surface area of a vacuum chamber is $2\,\text{m}^2$ and the outgassing constant is $1 \times 10^{-4}\,\text{Pa m}^3\,\text{s}^{-1}\,\text{m}^{-2}$ (not varying with time). N_2 is admitted at a rate of $2 \times 10^{-6}\,\text{Pa m}^3\,\text{s}^{-1}$.

(a) What is the pumping speed required to maintain 10^{-7} mbar in the system?

(b) If a pump having the speed required by (a) is attached to the system *via* a valve with an internal diameter of 300 mm, is the pressure achievable?

(c) By baking, the outgassing rate is reduced to $2 \times 10^{-6}\,\text{Pa m}^3\,\text{s}^{-1}$. What pumping speed is now necessary to achieve the same pressure?

(a)

$$q_{pV,\text{outg}} = 2 \times 10^{-4}\,\text{Pa m}^3\,\text{s}^{-1} = 2 \times 10^{-3}\,\text{mbar L s}^{-1}$$

$$q_{pV,\text{N}_2} = 2 \times 10^{-6}\,\text{Pa m}^3\,\text{s}^{-1} = 2 \times 10^{-5}\,\text{mbar L s}^{-1}$$

$$\therefore \quad q_{pV,\text{total}} = 2.02 \times 10^{-3}\,\text{mbar L s}^{-1}$$

Since $$p = \frac{q_{pV,\text{tot}}}{S_{\text{eff}}}$$

$$\therefore \quad \text{Required } S_{\text{eff}} = \frac{2.02 \times 10^{-3}\,\text{mbar L s}^{-1}}{10^{-7}\,\text{mbar}}$$

$$= \underline{2.02 \times 10^{4}\,\text{L s}^{-1}}$$

(b) Assume the conductance of the valve under high vacuum conditions is equivalent to an orifice of 300 mm diameter. For air under molecular flow conditions:

From Equation (2.23):

$$C_{\mathrm{or,air}} = 11.6\,A\ \mathrm{L\,s^{-1}}$$

In this case:

$$A = 707\ \mathrm{cm^2}$$
$$\therefore\quad C_{\mathrm{or,air}} = 8200\ \mathrm{L\,s^{-1}}\ (C_{\mathrm{or,air}} \cong C_{\mathrm{or,N_2}})$$

With outgassing, > 85% of the gas load is water vapour. From Equation (2.38):

$$C_{\mathrm{obj,B}} = C_{\mathrm{obj,A}}\sqrt{\frac{M_{\mathrm{B}}}{M_{\mathrm{A}}}}$$
$$\therefore\quad C_{\mathrm{or,H_2O}} = C_{\mathrm{or,air}}\sqrt{\frac{29}{18}}$$
$$= 10\,408\ \mathrm{L\,s^{-1}}$$

S_{eff} of the pump attached *via* the 300 mm valve can be calculated from Equation (2.5):

$$\frac{1}{S_{\mathrm{eff}}} = \frac{1}{S_{0,\mathrm{pump}}} + \frac{1}{C_{\mathrm{or}}}$$
$$\therefore\quad \frac{1}{S_{\mathrm{eff,N_2}}} = \frac{1}{20\,200} + \frac{1}{8200}$$
$$\therefore\quad S_{\mathrm{eff,N_2}} = 5831\ \mathrm{L\,s^{-1}}$$
$$\text{and}\quad S_{\mathrm{eff,H_2O}} = 6868\ \mathrm{L\,s^{-1}}$$

(assuming that $S_{0,\mathrm{pump}}$ is independent of gas type).
From this, it can be shown that $p_{\mathrm{tot}} = 2.93 \times 10^{-7}$ mbar.
Thus, the pressure in (a) is not attainable.

(c) After baking:

$$\begin{aligned} q_{pV,\mathrm{outg}} &= 2 \times 10^{-5}\ \mathrm{mbar\,L\,s^{-1}} \\ \underline{q_{pV,\mathrm{N_2}}} &\underline{= 2 \times 10^{-5}\ \mathrm{mbar\,L\,s^{-1}}} \\ q_{pV,\mathrm{tot}} &= 4 \times 10^{-5}\ \mathrm{mbar\,L\,s^{-1}} \end{aligned}$$

$$S_{\mathrm{eff}} = \frac{q_{pV,\mathrm{tot}}}{p}$$
$$= \frac{4 \times 10^{-5}\ \mathrm{mbar\,L\,s^{-1}}}{10^{-7}\ \mathrm{mbar}}$$
$$= \underline{400\ \mathrm{L\,s^{-1}}}$$

Example 4.27

A gas stream consisting of 4% H_2 in Ar is admitted to a vacuum chamber *via* a mass flow controller. The throughput is 5 sccm. The chamber is pumped by a turbomolecular pump ($S_0 = 100\,\text{L s}^{-1}$, independent of gas type). A throttle valve between the chamber and the TMP is used to control the chamber pressure. In the fully-open position, the conductance of this valve for Ar is 100 L s^{-1}. Is the gas composition maintained at the working pressure of the chamber if the valve is fully opened?

$$q_{pV,\text{tot,in}} = 5\,\text{sccm} \equiv \frac{5 \times 1013}{1000 \times 60}\,\text{mbar L s}^{-1}$$
$$= 0.084\,\text{mbar L s}^{-1}$$

$$q_{pV,\text{tot,in}} = q_{pV,\text{Ar}} + q_{pV,\text{H}_2}$$
$$= 0.96 q_{pV,\text{tot}} + 0.04 q_{pV,\text{tot}}$$
$$= 0.081\,\text{mbar L s}^{-1} + 3.36 \times 10^{-3}\,\text{mbar L s}^{-1}$$

$$S_{0,\text{TMP}} = 100\,\text{L s}^{-1}\ \text{(independent of gas type)}$$

Under conditions of molecular flow:

$$C_{\text{valve,Ar}} = 100\,\text{L s}^{-1} \neq C_{\text{valve,H}_2}$$

From Equation (2.38):

$$C_{\text{valve,H}_2} = 100\,\text{L s}^{-1} \times \sqrt{\frac{40}{2}}$$
$$= 447\,\text{L s}^{-1}$$

From Equation (2.5):

$$S_{\text{eff,TMP,Ar}} = 50\,\text{L s}^{-1}$$

and

$$S_{\text{eff,TMP,H}_2} = 82\,\text{L s}^{-1}$$

In the chamber:

$$p_{\text{tot}} = p_{\text{Ar}} + p_{\text{H}_2}$$
$$= \frac{q_{pV,\text{Ar}}}{S_{\text{eff,Ar}}} + \frac{q_{pV,\text{H}_2}}{S_{\text{eff,H}_2}}$$
$$= \frac{0.081\,\text{mbar L s}^{-1}}{50\,\text{L s}^{-1}} + \frac{3.36 \times 10^{-3}\,\text{mbar L s}^{-1}}{82\,\text{L s}^{-1}}$$

$$p_{\text{tot}} = 1.62 \times 10^{-3}\,\text{mbar} + 4.10 \times 10^{-5}\,\text{mbar} = 1.66 \times 10^{-3}\,\text{mbar}$$

So $$\underline{\frac{p_{H_2}}{p_{tot}} = \frac{4.10 \times 10^{-5}\,\text{mbar}}{1.66 \times 10^{-3}\,\text{mbar}} \cong 2.5\%\ (\text{not } 4\%)}$$

i.e. composition is not maintained.

However, if:

$$S_{H_2} = S_{Ar,}$$

$$\begin{aligned} p_{tot} &= 1.62 \times 10^{-3}\,\text{mbar} + 6.72 \times 10^{-5}\,\text{mbar} \\ &= 1.68 \times 10^{-3}\,\text{mbar} \end{aligned}$$

and

$$\underline{\frac{p_{H_2}}{P_{tot}} \simeq 4\%}$$

CHAPTER 5

Total and Partial Vacuum Pressure Measurement

5.1 INTRODUCTION

This chapter begins by looking at the measurement of total pressure in vacuum systems. The procedures and methods for pressure measurement throughout the vacuum range (1 bar to 10^{-13} mbar) are introduced. Important characteristics (including sensitivities to various gases) of some vacuum gauges are discussed in detail and illustrated by relevant examples.

The identification and quantification (partial pressure measurement) of the gaseous components in vacuum systems is of increasing importance in vacuum technology. This is achieved by the widely applied method of residual gas analysis. The simple theory of this is stated and relevant examples illustrate the application.

5.2 TOTAL PRESSURE MEASUREMENT

Introductory comments on pressure were made in Section 2.1. Particularly important is the fact that the pressure of gas in a system is a convenient expression of the particle number density (n) in that system (see Equation (1.5)).

There are two general procedures for pressure measurement: *direct* and *indirect*.

Direct methods are based on the fact that the force that constitutes pressure can physically shift a surface to which it is applied. Indirect methods monitor either the particle number density or a property of the gas that depends on n. Direct methods yield pressure information that is independent of the nature of the gas whilst pressures indicated by indirect methods are dependent on gas type. The need to have the two methods arises from the fact that, at low pressure, the forces involved are extremely low, and direct measurement becomes difficult if not impossible.

5.2.1 Direct Pressure Measurement

This can be carried out using a range of devices (Figure 5.1).

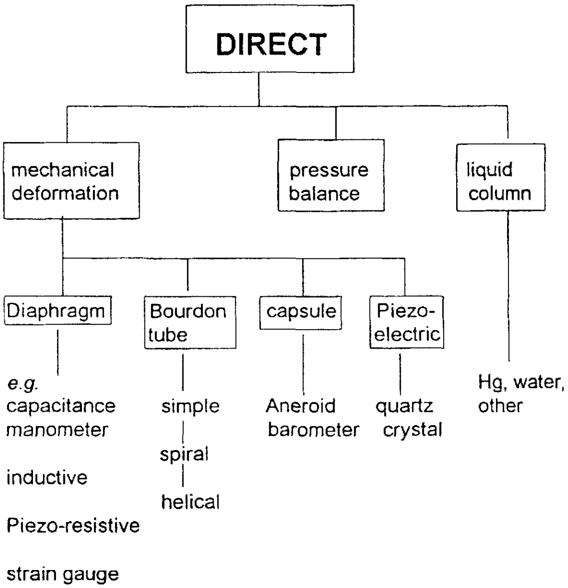


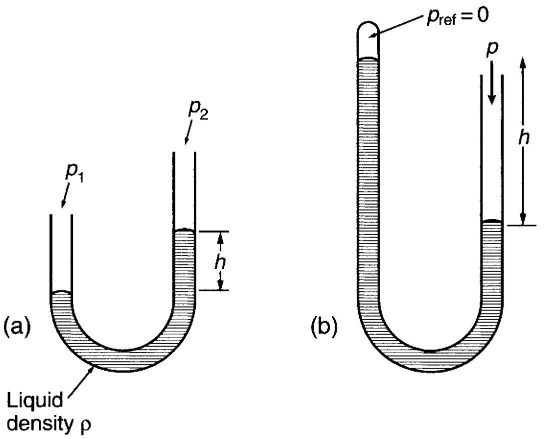
Figure 5.1 *Instruments used for direct pressure measurement*
(Reproduced from ref. (k) with permission of the Institute of Measurement and Control)

Manometers consisting of liquid columns of, commonly, mercury or a fluid such as silicone oil, have been used extensively in the past to measure gas mixtures in, for example, experimental, static investigations of the overall kinetics of gas-phase reactions. They continue to be used in many applications, including the establishment of primary pressure standards in several countries.

A simple manometer consists of a glass U-tube filled with a liquid of density ρ (see Figure 5.2).

Example 5.1

(a) If, in Figure 5.2 (b), the reference side of the manometer is evacuated to a negligibly low pressure by means of a valve leading to a vacuum system and the liquid in the manometer is mercury ($\rho_{\mathrm{Hg},\ 0\,°\mathrm{C}} = 13.595\,\mathrm{g\,cm^{-3}}$), calculate h if normal atmospheric pressure is applied to the open side ($g = 9.80665\,\mathrm{m\,s^{-2}}$).



$$p_1 - p_2 = h\rho g \quad (5.1) \qquad p_1 - p_{\text{ref}} = h\rho g \quad (5.2)$$

Where h is the difference in height between the two levels and g is the local acceleration due to gravity.

Figure 5.2 *U-tube manometer configuration: (a) open type; (b) closed type*

(b) If a similar manometer is being considered but using silicone oil ($\rho_{25\,^\circ\text{C}} = 1.07\ \text{g cm}^{-3}$) as the fluid, calculate h when normal atmospheric pressure is applied.

(a)

$$p = h\rho g$$

$$p_{\text{n}} = 101\,325\ \text{N m}^{-2}$$

$$\therefore \quad h = \frac{p}{\rho \times g} = \frac{101\,325\ \text{N m}^{-2}}{9.80665\ \text{m s}^{-2} \times 13.595 \times 10^3\ \text{kg m}^{-3}}$$

$$= 0.760\ \text{m}$$

$$\underline{= 760.00\ \text{mm}}$$

(b)

$$h = \frac{p}{\rho g}$$

$$= \frac{101\,325\ \text{N m}^{-2}}{9.80665\ \text{m s}^{-2} \times 1.07 \times 10^3\ \text{kg m}^{-3}}$$

$$\underline{= 9.66\ \text{m}}$$

A much more convenient method of direct pressure measurement involves the deflexion of a sensing element (*e.g.* a tensioned diaphragm made of a suitable metal or ceramic or a Bourdon tube) which separates the system from a reference volume. The force (F) on the sensing element (area A) gives rise to its deflexion:

$$F = (p_{\mathrm{sys}} - p_{\mathrm{ref}})A \tag{5.3}$$

and the deflexion may be estimated mechanically (as in simple Bourdon tube gauges) or electrically (as in capacitance diaphragm gauges).

In appropriate applications, capacitance diaphragm gauges (capacitance manometers) now replace liquid-in-tube manometers and Bourdon-type devices. (The exception is the use of manometers as primary pressure standards.) The principle is used for pressure measurement in the range 10s of bar down to 10^{-4} mbar, although a single head can only be used for low uncertainty measurement over four decades. For the highest precision in vacuum technology, temperature-controlled heads are available with full-scale readings in the range 10^3 mbar to 1 mbar.

Example 5.2

A mercury-in-glass manometer consists of a length of glass tubing (l = 100 cm, d = 1.3 cm). When evacuated at 20 °C, the height of the mercury in the tube is 750 mm. When isolated from the pumps, air leaks into the manometer and over a period of 2 h 47 min, the level falls to 650 mm. Assuming the temperature remains constant, calculate the air in-leakage in mbar L s^{-1} (density of mercury = 13.545 8 g cm^{-3} at 20 °C).

Height of mercury column changes from 750 to 650 mm

$$\therefore \quad \Delta p = h\rho g = 0.1\ \mathrm{m} \times 13.5458 \times 10^3\ \mathrm{kg\,m^{-3}} \times 9.80665\ \mathrm{m\,s^{-2}}$$

$$= 1.328 \times 10^4\ \mathrm{Pa}$$

$$= 132.8\ \mathrm{mbar}$$

Volume of gas in which pressure change has occurred

$$= \pi r^2 h$$

where h = length of gas column between mercury level and point of isolation from system (100 – 65 = 35 cm)
r = 0.65 cm
$\therefore \quad V = 46.46\ \mathrm{cm}^3$

$$\therefore \quad \text{Gas accumulation} = \frac{46.46 \times 132.8}{10^3} \text{ mbar } L \text{ in } 10^4\text{s}$$

$$\therefore \quad \underline{\text{Air in-leakage} = 6.2 \times 10^{-4}\,\text{mbar L s}^{-1}}$$

Example 5.3

Two types of direct pressure measuring gauges are available for measurement in the range 1 mbar to 100 mbar. One measures the deflexion of a diaphragm piezoresistively. It has a full-scale reading of 200 mbar and the measurement uncertainty is 0.2% full-scale. The second gauge is a capacitance diaphragm gauge with a full-scale deflexion of 1330 mbar and an uncertainty of 0.2% of the reading. Which is the more precise for pressure measurement in the required range? (Common methods of expressing uncertainty taken from ref. (k) with permission.)

A summary of the gauge characteristics is given below:

	Piezoresistive gauge FS = 200 mbar Uncertainty = 0.2% FS		Capacitance diaphragm gauge FS = 1330 mbar Uncertainty = 0.2% reading	
Pressure reading (mbar)	Uncertainty (mbar)	Percentage equivalent of reading	Uncertainty (mbar)	Percentage equivalent of FS reading
1	0.4	40	2×10^{-3}	$<10^{-3}$
10	0.4	4	0.02	10^{-3}
100	0.4	0.4	0.2	0.02

Clearly the CDG is the more precise in the range considered.

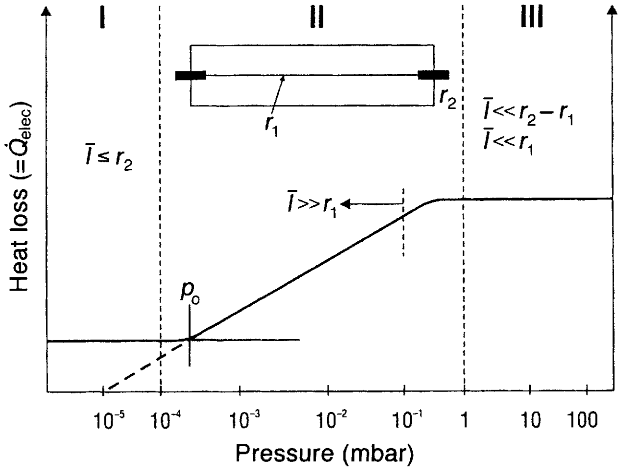
5.2.2 Indirect Pressure Measurement

5.2.2.1 Thermal Conductivity Vacuum Gauges. A very widely applied gauge of this type is the Pirani gauge. Such gauges consist of a wire (Pt, W or Ni, d = 5–20 μm; $l \sim 5$ cm) mounted axially in a cylindrical tube ($d \sim 2$ cm). The wire is heated by an electric current to approximately 100 °C above the ambient temperature and heat loss occurs by three mechanisms, as indicated in Figure 5.3.

Example 5.4

(a) Sketch a simple Pirani-type thermal conductivity gauge head and describe the principle of operation.

(b) Indicate typical applications of such gauges.



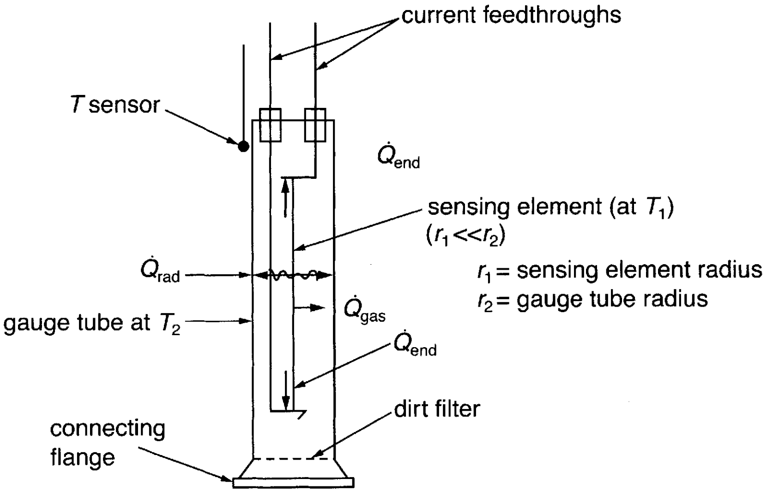
I = heat loss due predominantly to thermal radiation and conduction through wire supports

II = heat loss proportional to pressure

III = p-independent heat loss due to convection and radiation

Figure 5.3 *Pressure dependence of the heat loss from a heated wire (radius, r_1) in a tube (radius, r_2) at a constant temperature (ref. (e))*

(a)



The sensing element (usually a fine W or Pt wire) is heated to a temperature that is approx. 100 °C above that of its surroundings by an electric current. Heat is lost from the wire according to the mechanisms indicated ($\dot{Q}_{gas}$, $\dot{Q}_{rad}$ and $\dot{Q}_{end}$). $\dot{Q}_{rad}$ and $\dot{Q}_{end}$ are pressure-independent effects that simulate a heat loss even when $p = 0$ ($\dot{Q}_{\text{end}} + \dot{Q}_{\text{rad}} = S\,p_0$). $\dot{Q}_{\text{gas}}$ *is* pressure-dependent in a restricted range and can be represented as:

$$\dot{Q}_{\text{gas}} = S \cdot \frac{p}{1 + gp} \tag{5.4}$$

where S = a constant (gauge sensitivity) which depends on the properties of the gas

p = pressure

g = a factor to account for the geometrical arrangement of the gauge components.

If the sensing wire is at a constant temperature and the ambient temperature also remains constant, the electrical power to the wire:

$$\dot{Q}_{\text{elec}} = V \times I \tag{5.5}$$

is equal to the heat lost from the wire or:

$$\dot{Q}_{\text{elec}} = V_{\text{wire}}^2/R_{\text{wire}} = S\left(p_0 + \frac{p}{1 + gp}\right) \tag{5.6}$$

If $\dot{Q}_{\text{elec}}$ or some related quantity is measured and electrically supplied to the sensing element, the dependence on p is as shown (see Figure 5.3).

Pirani gauges are usually operated with a constant sensing element temperature (and hence constant R_{wire}) and the power required to maintain the constant temperature is measured. This can be carried out by having the wire as part of a Wheatstone-bridge-type circuit where the voltage to the bridge is controlled by an amplifier so that R_{element} remains constant. In practice, the bridge is slightly unbalanced and the voltage (V_{l}) applied to the bridge is indicated. The relationship between V_{l} and p is then given by:

$$V_{\text{l}} = \sqrt{R_{\text{element}}\, S\left(p_0 + \frac{p}{1 + gp}\right)} \tag{5.7}$$

This gives a non-linear scale with a zero pressure at about 10^{-2} mbar.

Using a more complex electronic circuit, the zero pressure (with the sensing head at $p < 10^{-3}$ mbar) may be compensated for with a zero-adjustment potentiometer. The required temperature of the wire (and hence S) is adjusted by another potentiometer (atmospheric pressure adjustment). By using these two potentiometers, adjustments can be made so that gauge heads are interchangeable and may be connected to any suitable power supply.

(b) Although Pirani gauges can indicate pressures between 10^3 and about 10^{-3} mbar, their usefulness is restricted to pressures between approximately 100 mbar and 10^{-3} mbar. The uncertainties in the measurements are: $\leq 20\%$ of the measured value in the range 10^{-3} to 10^{-2} mbar and $\leq 15\%$ of the measured value in the range 10^{-2} to 10^2 mbar. Pirani gauges are most widely used in the medium vacuum range. Specific applications include the monitoring and control of backing-line pressure in, for example, diffusion- and turbomolecular-pumped systems. They are also useful in monitoring the pressure during regeneration of cryopumps.

Further, since Pirani gauges working with a constant sensing-wire temperature have short response times (a few 10s of milliseconds) and provide 0–10 V outputs, they have general use in pressure control.

Example 5.5

(a) Does the indicated pressure on a thermal conductivity vacuum gauge depend on the gas and, if so, why?
(b) A Pirani-type gauge, adjusted and calibrated using N_2, is being used to measure H_2 at a pressure of 1 mbar. Will the indicated pressure be different from this?

(a) The indicated pressure is dependent on the type of gas because of the different thermal conductivities of the gases. For example, at 20 °C and standard atmospheric pressure, the thermal conductivity of H_2 is $0.183\,\mathrm{W\,m^{-1}\,K^{-1}}$ whilst that of N_2 is $2.55 \times 10^{-2}\,\mathrm{W\,m^{-1}\,K^{-1}}$ (see ref. (d) for example).
(b) Since the thermal conductivity of H_2 is significantly greater than that of N_2, more heat will be lost from the sensing element by conduction through H_2 than N_2 at the same pressure. The indicated H_2 pressure will therefore be higher than the actual pressure.

5.2.2.2 Ionisation Gauges. An ionisation gauge measures the pressure in a system by ionising a fraction of the gas particles from the system. Ionisation by electron impact is used, the electrons being generated either thermionically ('hot cathode' gauges) or in a magnetically sustained gas discharge ('cold cathode' gauges). An electrical quantity proportional to n (the particle number density) is measured. For hot cathode gauges, this is the ion current. For cold cathode gauges, the discharge current is measured.

Hot cathode ionisation gauges. The basic hot cathode ionisation gauge is shown in Figure 5.4. A heated cathode (C) emits a current of electrons (I^-) that is accelerated through a voltage between the cathode (U_C) and the anode (U_A) at a more positive potential. Electrons acquire energy according to $U_A - U_C$. They collide with gas particles, which may be

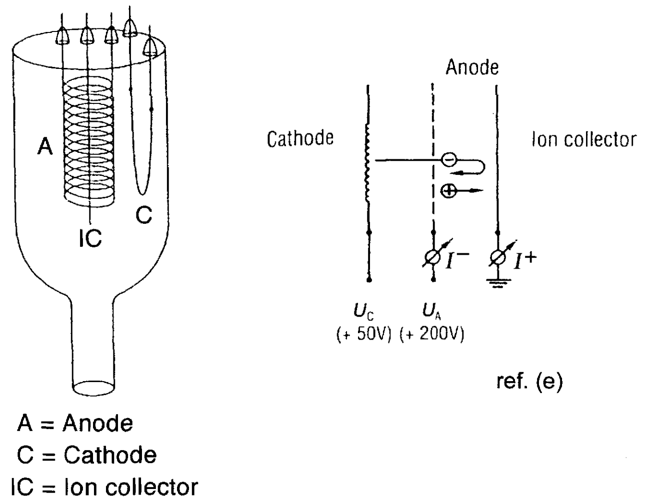


Figure 5.4 *Schematic diagram of a hot cathode ionisation gauge of the Bayard–Alpert type*

ionised as a result. Positive ions formed in this way travel to the collector (IC), which is negatively biased with respect to C and A, and the ion current (I^+) is measured.

If N^- electrons pass from cathode to anode (path length, l) through a gas of particle number density (n) and collision cross-section σ (dependent on the type of gas and the electron energy), some of the particles will be ionised.

If ΔN^- ionising collisions take place then:

$$\Delta N^- = N^- \times n \times \sigma \times l \tag{5.8}$$

and as many positive ions will be formed as successful electron collisions ($\Delta N^- = \Delta N^+$).

The quantity:

$$\frac{\Delta N^-}{N^- \times l} = n\sigma \tag{5.9}$$

indicates the number of ion pairs formed per electron per unit of path length through the gas of particle number density n.

Dividing by time, Equation (5.8) gives:

$$\frac{\Delta N^+}{t} = \frac{\Delta N^-}{t} = \frac{N^-}{t} \times n \times \sigma \times l$$

or

$$I^+ = I^- \times n\sigma l \tag{5.10}$$

Since:

$$p = nkT$$

then

$$I^+ = I^- \times \frac{\sigma l p}{kT} = I^- K p \tag{5.11}$$

where K is the gauge constant. K is dependent on several factors including the type of gas and the gauge geometry. It is determined experimentally.

Equation (5.10) can also be written:

$$I^+ = I^- \times s \times l \tag{5.12}$$

where $s = n\sigma$.

s is termed the 'differential ionisation'. In Equation (5.11), $I^- K$ is often symbolised as S and termed the 'sensitivity' of the ionisation gauge (see Equation (5.4).

Example 5.6

A hot cathode ionisation gauge has a gauge constant for N_2 of 10 mbar^{-1}. For an electron current of 1 mA, what is the ion current at 10^{-7} mbar?

From Equation (5.11):

$$\begin{aligned} & I^+ = I^- K p \\ \therefore\quad & I^+ = 1 \times 10^{-3} A \times 10\,\text{mbar}^{-1} \times 10^{-7}\,\text{mbar} \\ & \underline{= 10^{-9}\,\text{A}} \end{aligned}$$

Example 5.7

A hot cathode ionisation gauge has a gauge constant of 5 mbar^{-1} for N_2.

(a) For an electron current of 1 mA and an ion current of 2×10^{-8} A what is the pressure in a vacuum system containing only N_2?

(b) For the same pressure, what ion current would arise if the electron current fell to 0.1 mA?

(a) From Equation (5.11):

$$p = \frac{I^+}{I^- K} = \frac{2 \times 10^{-8}\,\text{A}}{1 \times 10^{-3}\,\text{A} \times 5\,\text{mbar}^{-1}}$$
$$\underline{= 4 \times 10^{-6}\,\text{mbar}}$$

(b) From Equation (5.11):

$$I^+ = I^- K p$$
$$= 10^{-4}\,\text{A} \times 5\,\text{mbar}^{-1} \times 4 \times 10^{-6}\,\text{mbar}$$
$$\underline{= 2 \times 10^{-9}\,\text{A}}$$

Note: It is usual with hot cathode ionisation gauges to keep I^- constant by controlling the cathode otherwise it would change due to surface effects such a gas coverage.

The ion yield (and hence I^+) for hot cathode ionisation gauges depends on the type of gas involved since some gases are easier to ionise than others. Indirect reading gauges are calibrated using N_2 as the reference gas. To obtain the actual pressure for gases other than N_2, the indicated pressure must be multiplied by a correction factor for the gas involved. Thus:

$$p_{\text{actual}} = p_{\text{indic}} \times \text{correction factor} \tag{5.13}$$

Approximate values for the correction factor are given in Table 5.1.

For gas mixtures (i-components), an *overall* factor can be obtained:

$$\frac{1}{\text{factor (overall)}} = \sum_i x_i \frac{1}{\text{corr. factor}_i} \tag{5.14}$$

where x is the mole fraction of the gas ($= n_i/n_{\text{tot}} = p_i/p_{\text{tot}}$)

Example 5.8

(a) An ionisation gauge, calibrated for air, reads 2×10^{-5} Pa. If the predominant gas is H_2, what is the actual pressure?

(b) If, in (a), the gas consisted of 20 v% Ar + 80 v% H_2, calculate p_{Ar} and p_{H2}.

(a) From Equation (5.13) and Table 5.1 (correction factor for H_2 is 2.4):

Table 5.1 *Some correction factors for the adjustment of indicated ionisation gauge pressure to gas type*

Gas	*Correction factor*[a]
N_2, air	1
He	6.9–7.1
Ar	0.83
Kr	0.59
H_2	2.4
D_2	2.5
CO_2	0.69
CO	0.92–0.95
CH_4	0.7–0.8
C_2H_6	0.4
oil vapours	0.1

[a] Actual values depend on gauge type and can be different particularly near gauge upper limit. (Reproduced from ref. (e), p. 82.)

$$\begin{aligned} p_{\text{actual}} &= 2 \times 10^{-5}\,\text{Pa} \times 2.4 \\ &= \underline{4.8 \times 10^{-5}\,\text{Pa}} \end{aligned}$$

Note: With a typical ionisation gauge, the uncertainty is approximately ±10% of the displayed value. This correction is greater than this.

(b) From Equation (5.14):

$$\frac{1}{\text{factor (overall)}} = x_{\text{Ar}}\frac{1}{0.83} + x_{\text{H}_2}\frac{1}{2.4}$$

$$= \frac{0.2}{0.83} + \frac{0.8}{2.4} = 0.57 \text{ (see Equation (1.9) and examples)}$$

$$\therefore \quad \text{factor (overall)} = 1/0.57 = 1.75$$

$$\begin{aligned} \therefore \quad p_{\text{actual}} &= 2 \times 10^{-5}\,\text{Pa} \times 1.75 \\ &= 3.5 \times 10^{-5}\,\text{Pa} \end{aligned}$$

and

$$p_{\text{Ar}} = \underline{x_{\text{Ar}}\, p_{\text{actual}} = 0.7 \times 10^{-5}\,\text{Pa}}$$

$$p_{\text{H}_2} = \underline{x_{\text{H}_2}\, p_{\text{actual}} = 2.8 \times 10^{-5}\,\text{Pa}}$$

Example 5.9

A chamber, fitted with an ionisation gauge calibrated for N_2, is evacuated with a turbomolecular pump ($S_{\text{eff}} = 150\,\text{L s}^{-1}$, independent of gas type).

(a) If N_2 is admitted to the chamber through a valve to establish a pressure of 10^{-3} Pa, what is the pV throughput for N_2?

(b) A mixture of $H_2 + N_2$ (1:5) is admitted through the valve to give an actual pressure of 10^{-2} Pa. What pressure will be indicated by the gauge assuming that the correction factor for H_2 is 2.4?

(a)

$$\begin{aligned} q_{pV,\mathrm{N_2}} &= p_{\mathrm{chamber}} \times S_{\mathrm{eff,TMP}} \\ &= 10^{-3}\,\mathrm{Pa} \times 150\,\mathrm{L\,s^{-1}} \\ &= \underline{0.15\,\mathrm{Pa\,L\,s^{-1}}} \end{aligned}$$

(b)

$$q_{pV,\mathrm{tot}} = q_{pV,\mathrm{H_2}} + q_{pV,\mathrm{N_2}} = 0.166 q_{\mathrm{tot}} + 0.833 q_{\mathrm{tot}}$$

where

$$q_{\mathrm{tot}} = p_{\mathrm{tot}} \times S_{\mathrm{eff}} = 10^{-2}\,\mathrm{Pa} \times 150\,\mathrm{L\,s^{-1}} = 1.5\,\mathrm{Pa\,L\,s^{-1}}$$

So

$$\begin{aligned} p_{\mathrm{tot}} &= p_{\mathrm{H_2}} + p_{\mathrm{N_2}} \\ &= \frac{q_{pV,\mathrm{H_2}}}{S_{\mathrm{eff}}} + \frac{q_{pV,\mathrm{N_2}}}{S_{\mathrm{eff}}} \\ &= \frac{0.166 \times 1.5\,\mathrm{Pa\,L\,s^{-1}}}{150\,\mathrm{L\,s^{-1}}} + \frac{0.833 \times 1.5\,\mathrm{Pa\,L\,s^{-1}}}{150\,\mathrm{L\,s^{-1}}} \\ &= 1.66 \times 10^{-3}\,\mathrm{Pa} + 8.33 \times 10^{-3}\,\mathrm{Pa} \end{aligned}$$

As indicated in Example 5.9, the gauge will indicate the H_2 contribution a factor 2.4 lower than actual.

$$\begin{aligned} \therefore \quad p_{\mathrm{tot,indic}} &= \frac{1.66 \times 10^{-3}\,\mathrm{Pa}}{2.4} + 8.33 \times 10^{-3}\,\mathrm{Pa} \\ &= 0.7 \times 10^{-3}\,\mathrm{Pa} + 8.3 \times 10^{-3}\,\mathrm{Pa} \\ &= \underline{9.0 \times 10^{-3}\,\mathrm{Pa}} \end{aligned}$$

Note: This calculation assumes $S_{\mathrm{eff,N_2}} = S_{\mathrm{eff,H_2}}$. If this is not the case then $\sum_i (q_{pV,i}/S_{\mathrm{eff},i})$ should be used.

A relationship exists between I^+ and the number of positively charged particles arriving at the collector:

$$I^+ = \frac{\Delta N^+}{\Delta t} ze \tag{5.15}$$

where ΔN^+ is the number of z-fold positively charged particles formed by N^- electrons and e is the elementary charge (1.6022×10^{-19}C).

For singly charged ions:

$$I^+ = \frac{\Delta N^+}{\Delta t} e$$

or

$$\frac{I^+}{e} = \frac{\Delta N^+}{\Delta t} = \frac{I^- K p}{e} \tag{5.15a}$$

Particularly at low pressures, errors may arise with hot cathode ionisation gauges because of two effects: the *X-ray effect* and *gas-ion desorption.*

The lowest measurable pressure is usually determined by the pressure-independent ion current which arises through initiation by soft X-rays generated by electron impact with the anode. These X-rays, in turn, cause a photoelectron current to be emitted by the collector. A pressure is therefore indicated by the gauge that is higher than the actual pressure:

$$p_{\text{ind}} = \frac{I^+ + I_r}{S} \tag{5.16}$$

where I_r is the residual, X-ray-initiated, photoelectron current. The X-ray limit of a gauge is the N_2 pressure where I_r is equal to the ion current.

Ion desorption effects arise as a result of electron impact on a gas-covered surface. In an ionisation gauge, if gas is adsorbed on the anode, this can be partly desorbed, as ions, by the impacting electrons. Such ions reach the collector and lead to a pressure indication that increases initially with electron current.

Example 5.10

(a) What is meant by the X-ray limit of a hot cathode ionisation gauge? How has consideration of the X-ray limit led to the development of ionisation gauges for the measurement of pressure below 10^{-7} mbar?

(b) A hot cathode ionisation gauge has a gauge constant of 0.09 Pa^{-1} for N_2 and an X-ray limit of 6×10^{-11} mbar. For an electron current of 10 mA, calculate the associated photoelectron current emitted by the collector.

(c) The gauge, calibrated for N_2, is attached to a system filled with H_2 to a pressure of 10^{-5} Pa. What will be the ion current for an emission current of 10^{-4} A?

(a) The X-ray limit is the N_2 pressure where the X-ray current is equal to the ion current.

From Equation (5.11):

$$I^+_{N_2} = I^- K p$$

At the X-ray limit:

$$I_r = I^+_{N_2}$$

Early hot cathode ionisation gauges were concentric triode gauges in which a central cathode was surrounded by a coaxial cylindrical ion collector. Because of the high X-ray limit, such gauges could only read down to 10^{-7} mbar. From Equation (5.16), it can be seen that the situation could be improved by lowering I_r.

In the gauge developed by Bayard and Alpert, I_r was decreased by reducing the surface area of the ion collector. In Bayard–Alpert gauges (BAGs), the collector is a thin wire surrounded by a cylindrical, coaxial open anode. With BAGs, pressures down to 10^{-9} mbar can be measured.

Reduction of I_r to even lower levels has been achieved with, for example, extractor ionisation gauges and measurements below 10^{-10} mbar can be made.

(b) At the X-ray limit:

$$I_r = I^+ = I^- K p$$

$$\therefore \quad I_r = 10^{-2}\,\text{A} \times 9\,\text{mbar}^{-1} \times 6 \times 10^{-11}\,\text{mbar}$$

$$= \underline{5.4 \times 10^{-12}\,\text{A}}$$

(c)

$$p_{H_2} = 10^{-5}\,\text{Pa}\ (10^{-7}\,\text{mbar})$$

$$I^+ = I^- K p \qquad \text{(Equation 5.11)}$$

$$= 10^{-4}\,\text{A} \times K_{H_2} \times 10^{-7}\,\text{mbar}$$

From Table 5.1:

$$K_{H_2} = \frac{K_{N_2}}{2.4}$$

$$\therefore \quad I^+ = 10^{-4}\,\text{A} \times \frac{9}{2.4}\,\text{mbar}^{-1} \times 10^{-7}\,\text{mbar}$$

$$= \underline{3.75 \times 10^{-11}\,\text{A}}$$

Example 5.11

A calibrated hot cathode ionisation gauge has $K_{N_2} = 0.09\,\mathrm{Pa}^{-1}$. In measurements on a system containing N_2 only, at 298 K, I^- is 10 mA.

(a) Derive a relationship between the N_2 pressure in the system and the number of particles (N) arriving at the collector as singly charged nitrogen molecule ions (N_2^+).
(b) Calculate the pV flow of N_2 corresponding to the (N_2^+) stream.
(c) If all the ions striking the collector are absorbed, calculate the pumping speed of the gauge.

(a) From Equation (5.15a):

$$\frac{I^+}{e} = \frac{N^+}{t} = \frac{I^- Kp}{e}$$

$$\therefore \quad \frac{N^+}{t} = \frac{10^{-2}\,\mathrm{A} \times 0.09\,\mathrm{Pa}^{-1} \times p}{1.602 \times 10^{-19}\,\mathrm{s\,A}}$$

$$\underline{= 5.62 \times 10^{15} p\,\mathrm{s}^{-1}\,\mathrm{Pa}^{-1}}$$

(b) Let q_{pV,N_2} be the pV flow of N_2 at the collector:

$$q_{pV,N_2} = \frac{p_{N_2} \times V}{t} = \frac{N^+ kT}{t}$$

From (a):

$$\frac{N^+}{t} = 5.62 \times 10^{15} p\,\mathrm{s}^{-1}\,\mathrm{Pa}^{-1}$$

$$\therefore \quad q_{pV,N_2} = 5.62 \times 10^{15} p\,\mathrm{s}^{-1}\,\mathrm{Pa}^{-1} \times 1.3807 \times 10^{-23}\,\mathrm{N\,m\,K}^{-1} \times 298\,\mathrm{K}$$

$$= 2.31 \times 10^{-5} p\,\mathrm{s}^{-1}\,\mathrm{N\,m\,Pa}^{-1}$$

As $1\,\mathrm{Pa} = 1\,\mathrm{N\,m}^{-2}$, this becomes

$$q_{pV,N_2} = 2.31 \times 10^{-5} p\,\mathrm{m}^3\,\mathrm{s}^{-1}$$

$$\underline{= 2.31 \times 10^{-2} p\,\mathrm{L\,s}^{-1}}$$

(c)

$$q_{pV,N_2} = S_{\mathrm{gauge}} \times p$$

where, in this equation, S_{gauge} denotes the pumping speed (in $\mathrm{L\,s}^{-1}$) of the gauge.

From (b):

$$q_{pV,N_2} = 2.31 \times 10^{-2} p \, \mathrm{L\,s^{-1}}$$

$$\therefore \quad S_{\text{gauge}} = \underline{2.31 \times 10^{-2} \, \mathrm{L\,s^{-1}}}$$

Example 5.12

A Bayard–Alpert gauge has a gauge constant for N_2 of 17 mbar^{-1}. The emission current can be altered from 0.06 to 0.6 mA.

(a) If the gauge is operating with $I^- = 0.6$ mA and is attached to a system containing pure N_2 at 298 K calculate the sensitivity of the gauge.

(b) Adsorbed gases can be desorbed by electron impact. For an ionisation in which each electron that reaches the anode leads to the desorption of N_2 molecules with a probability of 10^{-3}, what is the associated electron-induced pV flow?

(a) The term KI^- is often termed the sensitivity (S) of the gauge.
Note: S should not be confused with the pumping speed of the gauge (see Example 5.12).

In this case,

$$\begin{aligned} S &= KI^- \\ &= 17\,\mathrm{mbar^{-1}} \times 6 \times 10^{-4}\,\mathrm{A} \\ &= \underline{1.02 \times 10^{-2}\,\mathrm{A\,mbar^{-1}}} \end{aligned}$$

(b) N^- electrons pass from cathode towards the anode. In unit time this is N^-/t.

$$N^-/t = I^-/e$$

where e is the elementary charge.

If each electron gives rise to N_2 desorption with a probability of 10^{-3}:

$$\frac{N^-}{t} \times 10^{-3} = \frac{N_{\text{des}}}{t}$$

$$\therefore \quad \frac{I^-}{e} \times 10^{-3} = \frac{N_{\text{des}}}{t}$$

$$\therefore \quad \frac{N_{\text{des}}}{t} = \frac{6 \times 10^{-4}\,\mathrm{A} \times 10^{-3}}{1.602 \times 10^{-19}\,\mathrm{s\,A}} = 3.75 \times 10^{12}\,\mathrm{s^{-1}}$$

$$
\begin{aligned}
q_{pV} &= \frac{N_{\mathrm{des}}}{t} \times kT \\
&= 3.75 \times 10^{12}\,\mathrm{s^{-1}} \times 1.3807 \times 10^{-23}\,\mathrm{N\,m\,K^{-1}} \times 298\,\mathrm{K} \\
&= 1.54 \times 10^{-8}\,\mathrm{N\,m\,s^{-1}} \\
&\equiv 1.54 \times 10^{-8}\,\mathrm{Pa\,m^3\,s^{-1}} \\
&= \underline{1.54 \times 10^{-7}\,\mathrm{mbar\,L\,s^{-1}}}
\end{aligned}
$$

Note: If some of the gas is desorbed as ions and the ions reach the collector, the pressure indication is not p-dependent and rises as I^- increases. If a small I^- is used so that the number of electrons hitting the anode is small compared to the number of adsorbed gas particles, each electron can desorb positive ions. If I^- is then increased, N_{des} will increase and eventually deplete the adsorbed layer on the surface. The pressure indication then falls and can reach values lower than the pressure shown at small I^- values.

Whether or not the reading is influenced by a desorption current, I^- should be changed by a factor of 10–100 and the reading observed. The reading at the larger I^- is the more precise value.

Cold cathode ionisation gauges. In such gauges, a gas discharge is established between two unheated metal electrodes (anode and cathode) by means of a high (about 2 kV) DC voltage. It is maintained down to very low pressure using a strong (0.1–0.2 T) magnetic field. Within the discharge electrons exist which can participate in ionising collisions with gas particles. The crossed magnetic and electrical fields confine the electrons and considerably increase their path length.

The nature of the discharge depends on the pressure. For Penning gauges at $p < 10^{-2}$ Pa, it is sustained by a negative, circulating ring current (I_{R}) established in the cylindrical anode. The ring current has the same function as I^- in hot cathode ionisation gauges. Charge carriers produced in ionising collisions move to the corresponding electrodes and give a pressure-dependent discharge current (I_{D}) that serves as the measured quantity for pressure indication.

The useful pressure measuring range for cold cathode gauges is ~10^{-3} mbar to 10^{-9} mbar. By analogy to hot cathode gauges, the following relationship can be established:

$$I_{\mathrm{D}} = I_{\mathrm{R}} K_{\mathrm{cc}}\, p \qquad (5.17)$$

Values for K_{cc} are significantly higher than gauge constants for hot cathode ionisation gauges.

Example 5.13

The ring current in a Penning gauge at 298 K is 1 A. The measured sensitivity for N_2 for the gauge is 2 A mbar^{-1}. If all the ions striking the collector are absorbed, calculate the pumping speed of the cold cathode gauge.

$$I_{\mathrm{D}} = I_{\mathrm{R}} K_{\mathrm{cc}}\, p$$

The sensitivity of the gauge is given by analogy to Equation (5.11) as:

$$S = I_{\mathrm{R}} K_{\mathrm{cc}}$$

$$\therefore \quad K_{\mathrm{cc}} = 2\,\mathrm{mbar}^{-1}(0.02\,\mathrm{Pa}^{-1})$$

Gas consumption can be estimated by assuming that all the ions striking the cathode are implanted (absorbed) then, from Equation (5.15a):

$$\begin{aligned}\frac{\Delta N^+}{\Delta t} &= \frac{I_{\mathrm{R}} K_{\mathrm{cc}}\, p}{e}\\ &= \frac{1\,\mathrm{A} \times 0.02\,\mathrm{Pa}^{-1} \times p}{1.602 \times 10^{-19}\,\mathrm{s\,A}}\\ &= 1.25 \times 10^{17} p\,\mathrm{s}^{-1}\,\mathrm{Pa}^{-1}\end{aligned}$$

If S_{gauge} is the pumping speed of the gauge:

$$\begin{aligned}S_{\text{gauge}} &= \frac{\Delta N^+}{\Delta t}\frac{kT}{p}\\ &= \frac{1.25 \times 10^{17} p\,\mathrm{s}^{-1}\,\mathrm{Pa}^{-1} \times 1.3807 \times 10^{-23}\,\mathrm{N\,m\,K}^{-1} \times 298\,\mathrm{K}}{p}\\ &= 5.143 \times 10^{-4}\,\mathrm{m}^3\,\mathrm{s}^{-1}\\ &= \underline{0.51\,\mathrm{L\,s}^{-1}}\end{aligned}$$

As indicated in Chapter 4, sputter ion pumps are based on sorption processes initiated by gas ions formed in a Penning discharge and SIPs achieve their high pumping speed by incorporating many individual Penning cells.

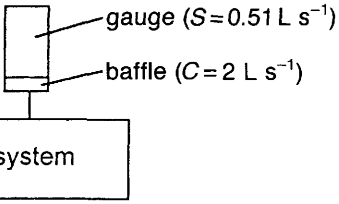
Because of gauge pumping, it is possible for ion gauges, particularly cold cathode types, to indicate a lower pressure reading than that of the system if a low conductance connection exists between the two. The pumping speed of a cold cathode gauge is significantly greater than that of a hot cathode ionisation gauge (see Example 5.11).

Example 5.14

The Penning gauge in Example 5.13 is fitted with a baffle ($C_{N_2} = 2\ \mathrm{L\,s^{-1}}$) to reduce gauge contamination, and attached to a vacuum system.

(a) Calculate the pressure in the system if the gauge indicates 5×10^{-5} mbar.
(b) Is the result significant?

(a)



The gauge will have an effective pumping speed ($S_{\mathrm{eff,gauge}}$) at the system side of the baffle given by

$$\frac{1}{S_{\mathrm{eff,gauge}}} = \frac{1}{S_0} + \frac{1}{C_{\mathrm{baff}}} = \frac{1}{0.51} + \frac{1}{2}$$

giving $S_{\mathrm{eff,gauge}} = 0.41\ \mathrm{L\,s^{-1}}$.

The continuity equation shows that:

$$p_{\mathrm{system}} \times S_{\mathrm{eff,gauge}} = p_{\mathrm{gauge}} \times S_{\mathrm{gauge}}$$

$$\therefore \quad p_{\mathrm{system}} \times 0.41\ \mathrm{L\,s^{-1}} = 5 \times 10^{-5}\ \mathrm{mbar} \times 0.51\ \mathrm{L\,s^{-1}}$$

$$\therefore \quad p_{\mathrm{system}} = \underline{6.2 \times 10^{-5}\ \mathrm{mbar}}$$

(b) Probably not. The accepted uncertainty in Penning gauge readings is about ±30%. The indicated pressure is such that the system pressure would be within the gauge uncertainty. Penning gauges, for this reason, tend to be used on systems where control of pressure levels is of more importance than precise pressure measurement.

5.3 RESIDUAL GAS ANALYSIS AND PARTIAL PRESSURE MEASUREMENT

Measurement of total pressure is insufficient for the characterisation of vacuum systems. Detailed information (system cleanliness, presence of leaks, *etc.*) can only be obtained by the identification of components present in the gas phase by means of residual gas analysis. Having established gas composition, however, the determination of partial pressures is relatively straightforward.

Most residual gas analysers (RGAs) used routinely on vacuum systems are based on quadrupole mass spectrometers (see Figure 5.5). They have a mass range starting at 1 amu and ending at 100 amu.

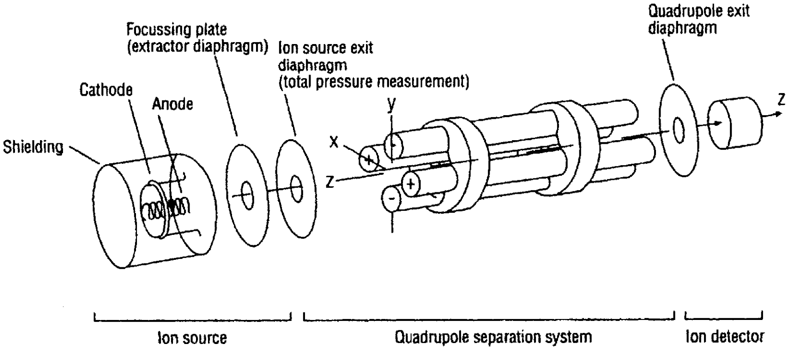


Figure 5.5 *Schematic diagram of an RGA based on a quadrupole mass spectrometer* (Reproduced from ref. (e), p. 82)

The RGA consists of three subsystems:

- the ion source (for generation of positive ions from the system gases)
- the mass-to-charge ratio filter (quadrupole separation system) in which a combination of DC and high-frequency AC voltages select ions with stable paths in the filter)
- the ion detector (ion currents associated with ions that pass the filter are measured at the detector).

An ion beam extracted from the ion source passes to the mass separation system where continuous changes in the voltages applied to the electrodes allow ions of the appropriate mass/charge (*M*/*Z*) ratio to achieve stability in the mass filter and pass to the detector. A spectrum is therefore generated giving the variation of the amplitude of the detector signal with M/Z. The M/Z value enables the mass fragment to be identified and the signal amplitude (as ion current I^+) indicates the amount of the species present.

As with the hot cathode ionisation gauge, there is a relationship between I^+ and gas pressure (see Equation 5.11) so the RGA sensitivity (S_{RGA}) can be expressed as:

$$S_{\text{RGA}} = \frac{I^+{}_{M/Z}}{p_{M/Z}} \tag{5.18}$$

The ionisation process does not reproduce, in the output of ions, the relative amount of gas at the source. By the use of reference gases, such as N_2, the gauge sensitivity can be established and, by the use of appropriate correction factors, differing extents of ionisation can be accounted for.

For a given electron energy, atoms and molecules may fragment during ionisation. The fragment distribution pattern (cracking pattern, fragmentation pattern) is often referred to as the 'fingerprint' of the starting species. An example of a fragmentation pattern is shown in Table 5.2. From these data, fragmentation factors (the portion of the total spectrum represented by a particular peak) may be calculated.

Example 5.15

Explain the presentation of the residual gas analysis data in Table 5.2. Calculate the fragmentation factors (FF) associated with the given peaks.

The mass spectrum of water vapour, according to Table 5.2, consists of five peaks. The largest is at 18 amu, the second largest at 17 amu, the third largest at 1 amu, *etc.* The signals associated with all peaks have been represented as a percentage of the amplitude of the largest peak, *e.g.* if the peak at 18 amu is 100%, the peak at 17 amu (the second largest) has an amplitude which is 25% of the largest peak and so on.

Table 5.2 *Fragment distribution pattern of water vapour for ionising electron energy = 102 eV*

Ion	*M/Z*	*Amplitude of the associated detector signal given as a percentage of the major peak (M/Z = 18)*
H_2O^+	18	100
OH^+	17	25
O^+	16	2
H_2^+	2	2
H^+	1	6 ($\Sigma\% = 135\%$)

(Reproduced from W. Umrath, ref. (e), p. 103)

To determine the portion of the total spectrum represented by a particular peak (the fragmentation factor), the normalised data are added together. The FF is then the relative percentage of the major peak divided by the total percentage. For example, the H_2O^+ peak represents (100/135) = 0.74 of the total spectrum; OH^+ represents (25/135) = 0.185 of the total spectrum, *etc.* These data are summarised below:

M/Z	FF
18	0.74
17	0.185
16	0.015
2	0.015
1	0.044
	$\Sigma = 99.9\%$

The nature of the fragments formed and their yield depends on the RGA geometry and, particularly, on the energy of the ionising electrons. This is shown in Table 5.3.

Table 5.3 *Fragment distribution pattern for several gases for different ionising electron energies*[a]

		Peaks in order of abundance[b]					
Substance		*1*	*2*	*3*	*4*	*5*	*6*
Ar	(a)	40(100)	20(33.1)	–	–	–	–
	(b)	40(100)	20(10)	36(0.3)			
H_2O	(a)	18(100)	17(27)	1(20)	2(8.4)	16(3.2)	19(2.3)
	(b)	18(100)	17(25)	1(6)	2(2)	16(2)	–
O_2	(a)	32(100)	16(17.8)	34(0.53)	–	–	–
	(b)	32(100)	16(11)	–	–	–	–
N_2	(a)	28(100)	14(15)	29(0.8)	–	–	–
	(b)	28(100)	14(7)	29(1)	–	–	–
CO_2	(a)	44(100)	16(16.1)	28(11.5)	12(8.4)	45(1.3)	–
	(b)	44(100)	28(11)	16(9)	12(6)	45(1)	22(1)
Mechanical pump oil	(a)	–	–	–	–	–	–
	(b)	43(100)	41(91)	57(73)	55(64)	71(20)	69(19)
TMP oil	(a)	–	–	-	–	–	–
	(b)	43(100)	57(88)	41(76)	55(73)	71(52)	69(49)

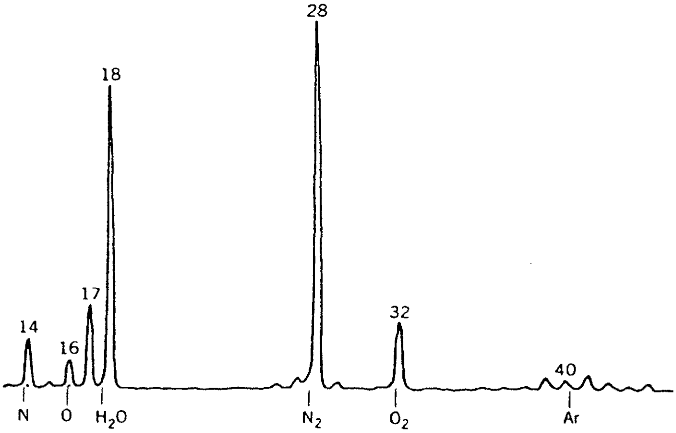
[a] (a) $E = 75$ eV, (b) $E = 102$ eV.

[b] Data presented as M(% major peak) (as Table 5.2)

(Reproduced from W. Umrath, ref. (e), p. 103)

Example 5.16

A mass spectrum obtained from an RGA attached to a vacuum vessel is shown below. Comment on the system.



The spectrum is dominated by the water peak at 18 (together with peaks at 17 and 16, see Table 5.2). The two peaks at 28 and 32 with a peak height ratio of approximately 5:1 indicate air leakage into the system since they correspond closely to the amounts of N_2 and O_2 in natural air. It is probable that the air leakage is introducing a significant amount of water vapour to the system although water vapour desorption from the walls ('virtual leakage') will also contribute.

Equation (5.18) gives the relationship between I^+ for a particular mass peak, the RGA sensitivity and the pressure of the species which gave rise to the mass peak. Almost all gases fragment during ionisation and to obtain partial pressure data from the mass peaks, two methods can be used:

(i) *all* the mass fragments (M_1, M_2, *etc.*) associated with the gas of interest (G) are identified and the sum of all the associated ion currents ($I^+_{M_1}$, $I^+_{M_2}$, *etc.*) giving the total ion current (I^+_{tot}) is obtained. Equation (5.18) can then be rearranged to give:

$$p_G = \frac{I^+_{\text{tot,G}}}{S_{\text{RGA,G}}} \tag{5.18a}$$

(ii) *one unambiguous mass fragment* (say M_G) is selected and the relevant ion current I^+_M measured. With the appropriate fragmentation factor (see Example 5.15 and Table 5.3) for M_G in relation to the total mass spectrum the relationship:

$$p_G = \frac{I^+_{M_G}}{FF_{M_G} S_G} \tag{5.19}$$

is found.

As stated before, the sensitivity of an RGA is established for a reference gas, *e.g.* N_2. Thus, in:

$$S_{N_2} = \frac{I^+_{N_2}}{p_{N_2}} \tag{5.20}$$

(where $I^+_{N_2}$ has been determined as given above; in method (ii), the peak $M = 28$ is generally selected), N_2 of the highest available purity is used and p_{N_2} measured with either a calibrated ion gauge or a spinning rotor gauge.

The sensitivity, S_G, of any gas G for an RGA can be found from a predetermined sensitivity (say S_{N_2}) from the relationship:

$$S_G = S_{N_2} \times RIP_G \tag{5.21}$$

where RIP_G is the ionisation probability of G relative to N_2.

Some values are given in Table 5.4. They are almost identical with the reciprocals of the ionisation gauge correction factors given in Table 5.1.

Table 5.4 *Ionisation probabilities relative to N_2 (for electron energies of 102 eV)*

Gas	*RIP*	*Gas*	*RIP*
N_2	1.0	C_2H_6	2.6
Ar	1.2	C_3H_8	3.7
CO_2	1.4	Ne	0.23
CO	1.05	NO	1.2
He	0.14	O_2	1.0
H_2	0.44	SO_2	2.1
H_2O	11.00	Xe	3.0
CH_4	1.6		

(Reproduced from W. Umrath, ref. (e), p. 103)

Example 5.17

A spectrum of pure Ar is obtained using an RGA operating with 75 eV electrons. It consists of two peaks at 40 amu and 20 amu. The RGA has $S_{N_2} = 1 \times 10^{-4}$ A mbar^{-1}.

(a) If $I_{20}^{+} = 2.3 \times 10^{-9}$ A and $I_{40}^{+} = 7 \times 10^{-9}$ A, calculate p_{Ar}.
(b) Calculate p_{Ar} using the I_{40}^{+} measurement alone.

(a) From Equation (5.18a):

$$p_{\mathrm{Ar}} = \frac{(I_{\mathrm{Ar},40}^{+} + I_{\mathrm{Ar},20}^{+})}{S_{\mathrm{Ar}}}$$

From Equation (5.21):

$$S_{\mathrm{Ar}} = S_{\mathrm{N_2}} \times 1.2$$

$$\therefore \quad p_{\mathrm{Ar}} = \frac{9.3 \times 10^{-9}\,\mathrm{A}}{1 \times 10^{-4}\,\mathrm{A\,mbar^{-1}} \times 1.2}$$

$$\underline{= 7.8 \times 10^{-5}\,\mathrm{mbar}}$$

(b) From Equation (5.19):

$$p_{\mathrm{Ar}} = \frac{I_{\mathrm{Ar},40}^{+}}{\mathrm{FF}_{\mathrm{Ar},40} \times S_{\mathrm{Ar}}}$$

From the data in Table 5.3:

$$\mathrm{FF}_{\mathrm{Ar},40} = \frac{100}{133.1} = 0.75$$

$$\therefore \quad p_{\mathrm{Ar}} = \frac{7 \times 10^{-9}\,\mathrm{A}}{0.75 \times 1.2 \times 10^{-4}\,\mathrm{A\,mbar^{-1}}}$$

$$\underline{= 7.8 \times 10^{-5}\,\mathrm{mbar}}$$

Example 5.18

A vacuum vessel, fitted with an RGA, is pumped down to 8×10^{-6} mbar with a TMP with $S_{\mathrm{eff}} = 150\,\mathrm{L\,s^{-1}}$ (independent of gas type). No leakage can be found on the system. If the system develops a leak and an in-leakage of atmospheric air of 1×10^{-2} mbar L s^{-1} occurs,

(a) what would be the resulting total pressure?
(b) what changes in the spectrum at 28 and 32 amu might be seen? Assume that the RGA has $S_{\mathrm{N_2}} = 1 \times 10^{-4}\,\mathrm{A\,mbar^{-1}}$ and $E_{\mathrm{e^-}} = 102$ eV.

(a) Base pressure for the vessel is 8×10^{-6} mbar.
With $S_{\mathrm{eff}} = 150\,\mathrm{L\,s^{-1}}$, gas load $= p_{\mathrm{base}} \times S_{\mathrm{eff}}$

$$= 1.2 \times 10^{-3}\,\mathrm{mbar\,L\,s^{-1}}$$

With air in-leakage of 1×10^{-2} mbar L s^{-1}, the total gas load,

$$\begin{aligned} q_{\text{tot}} &= 1.2 \times 10^{-3}\,\text{mbar L s}^{-1} + 10^{-2}\,\text{mbar L s}^{-1} \\ &= 11.2 \times 10^{-3}\,\text{mbar L s}^{-1} \\ \therefore\quad p_{\text{tot}} = \frac{q_{\text{tot}}}{S_{\text{eff}}} &= \frac{11.2 \times 10^{-3}}{150}\,\text{L s}^{-1} \\ &= \underline{7.5 \times 10^{-5}\,\text{mbar}} \end{aligned}$$

(b) If the initial gas load (1.2×10^{-3} mbar L s^{-1}) consisted of 80% water vapour with the remainder being O_2 and N_2 with a composition normally found in atmospheric air then:

$$q_{\text{in}} = q_{H_2O} + q_{N_2+O_2} = 9.6 \times 10^{-4}\,\text{mbar L s}^{-1} + 2.4 \times 10^{-4}\,\text{mbar L s}^{-1}$$

If $q_{N_2+O_2}$ consists of 78.1 v% N_2 and 20.9 v% O_2, then

$$\begin{aligned} q_{N_2} &= 0.781 \times 2.4 \times 10^{-4} = 1.87 \times 10^{-4}\,\text{mbar L s}^{-1} \\ q_{O_2} &= 0.209 \times 2.4 \times 10^{-4} = 5.02 \times 10^{-5}\,\text{mbar L s}^{-1} \end{aligned}$$

So

$$\begin{aligned} p_{N_2} &= \frac{1.87 \times 10^{-4}\,\text{mbar L s}^{-1}}{150\,\text{L s}^{-1}} = 1.25 \times 10^{-6}\,\text{mbar} \\ p_{O_2} &= \frac{5.02 \times 10^{-5}\,\text{mbar L s}^{-1}}{150\,\text{L s}^{-1}} = 3.35 \times 10^{-7}\,\text{mbar} \end{aligned}$$

In the region of 28 and 32 amu, the RGA spectrum (without air in-leakage) would have a signal:

$$\begin{aligned} I_{N_2^+,28} &= p_{N_2} \times \text{FF}_{N_2,28} \times S_{N_2} \\ &= 1.25 \times 10^{-6}\,\text{mbar} \times 0.93 \times 1 \times 10^{-4}\,\text{A mbar}^{-1} \\ &= 1.2 \times 10^{-10}\,\text{A} \\ I_{O_2^+,32} &= 3.35 \times 10^{-7}\,\text{mbar} \times 0.90 \times 1 \times 10^{-4}\,\text{A mbar}^{-1} \\ &= 3.1 \times 10^{-11}\,\text{A} \end{aligned}$$

With an air in-leakage of 1×10^{-2} mbar L s^{-1}:

$$q_{N_2} = 0.781 \times 1.10^{-2}\,\text{mbar L s}^{-1} = 7.81 \times 10^{-3}\,\text{mbar L s}^{-1}$$

$$q_{O_2} = 0.209 \times 1.10^{-2}\,\text{mbar L s}^{-1} = 2.09 \times 10^{-3}\,\text{mbar L s}^{-1}$$

So $p_{N_2} = 5.2 \times 10^{-5}\,\text{mbar}$

and $p_{O_2} = 1.39 \times 10^{-5}\,\text{mbar}$

In the region of 28 and 32 amu, the RGA signal would increase to:

$$\begin{aligned} I^{+}_{N_2,28} &= p_{N_2} \times FF_{N_2,28} \times S_{N_2} \\ &= 5.2 \times 10^{-5}\,\text{mbar} \times 0.93 \times 1 \times 10^{-4}\,\text{A mbar}^{-1} \\ &= 4.8 \times 10^{-9}\,\text{A} \\ I^{+}_{O_2,32} &= 1.39 \times 10^{-5}\,\text{mbar} \times 0.90 \times 1 \times 10^{-4}\,\text{A mbar}^{-1} \\ &= 1.25 \times 10^{-9}\,\text{A} \end{aligned}$$

Before the air in-leakage, it would be difficult, without an electron multiplier, to observe the peaks at 28 and 32 amu. With the air in-leakage, the ion currents at 28 and 32 amu would be easily measurable.

CHAPTER 6

Some Applications of Vacuum Technology

6.1 INTRODUCTION

This chapter examines some areas in which vacuum technology is applied to the chemical sciences. Firstly, unit operations such as drying and distillation, of importance in chemical technology, are discussed. The use of condensers in association with vacuum pumps is introduced and typical calculations demonstrated.

Secondly, the use of UHV/EHV systems is obviously desirable because of the extreme sensitivity of many materials and processes to residual gas. Work in this pressure range has allowed significant advances to be made in, for example, surface science and the exploitation in many areas of research of synchrotron radiation sources based on electron or positron storage rings. Relevant factors in the operation of these systems, such as adsorption and desorption (including diffusive outgassing), are examined in detail.

Thirdly, the use of differential pumping, as a general technique, is examined. It is widely applied in systems where regions having large pressure differentials are interfaced. Specific systems are discussed to indicate the usefulness of the technique.

6.2 CHEMICAL TECHNOLOGY

The application of vacuum conditions in chemical technology lies not in the performance of chemical reactions but in the treatment and purification of reactants and products. This may often involve thermal processing such as distillation and drying.

6.2.1 Pressure, Temperature and Phase Changes

The advantage of carrying out thermal processes under vacuum pressures can be seen if the liquid–gas boundary is considered.

The Clapeyron equation states the relationship between a phase change for a pure material and changes in pressure and temperature. For vaporisation:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{vap,m}}}{T(v_{\mathrm{vap,m}} - v_{l,\mathrm{m}})} \tag{6.1}$$

where $v_{\mathrm{vap,m}}$ and $v_{l,\mathrm{m}}$ are the molar volumes of the vapour and liquid, respectively and $\Delta H_{\mathrm{vap,m}}$ is the molar enthalpy of vaporisation.

Example 6.1

Using the Clapeyron equation, calculate the enthalpy of vaporisation (evaporation) of water from the following data:

$T_{\mathrm{boiling,1\,atm}}$ = 100 °C

$\mathrm{d}p/\mathrm{d}T$ = 3614 Pa K^{-1}

density of water = 0.962 g cm^{-3}

density of water vapour = 5.973×10^{-4} g cm^{-3}

From Equation (6.1):

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{vap}}}{T_{\mathrm{b}}(v_{\mathrm{vap}} - v_l)}$$

where T_{b} is the boiling point of water at $p = 1$ atm and v_{vap} and v_l are the specific volumes (volumes per unit mass) of water vapour and liquid water, respectively.

From the given data:

density of liquid water = 962 kg m^{-3}

$$\therefore \quad v_l = 1.04 \times 10^{-3}\,\mathrm{m^3\,kg^{-1}}$$

density of water vapour = 0.5973 kg m^{-3}

$$\therefore \quad v_{\mathrm{vap}} = 1.6742\,\mathrm{m^3\,kg^{-1}}$$

$$\therefore \quad \Delta H_{\mathrm{vap}} = \frac{\mathrm{d}p}{\mathrm{d}T} \times T_{\mathrm{b}}\,(v_{\mathrm{vap}} - v_l)$$

$$= 3614\,\text{Pa K}^{-1} \times 373\,\text{K} \times (1.6742 - 0.00104)\,\text{m}^3\,\text{kg}^{-1}$$
$$= 2255.46\,\text{kJ kg}^{-1}$$
$$\underline{= 40.60\,\text{kJ mol}^{-1}}$$

As v_{vap} is much larger than v_l, in Equation (6.1) $(v_{\text{vap}} - v_l)$ can be replaced by $v_{\text{vap,m}}$, where the subscript 'm' refers to a unit amount (mol^{-1}, kmol^{-1}), or, better, $v_{\text{m}}(\text{vap})$. If it is assumed that the vapour behaves ideally ($v_{\text{m}} = RT/p$), then the Clausius–Clapeyron equation is obtained:

$$\frac{\mathrm{d}(\ln p)}{\mathrm{d}T} = \frac{\Delta H_{\text{vap,m}}}{RT^2} \tag{6.2}$$

If it is further assumed that $\Delta H_{\text{vap,m}}$ does not depend on temperature then Equation (6.2) integrates to:

$$\ln p = \text{const} - \frac{\Delta H_{\text{vap,m}}}{RT} \tag{6.3}$$

or

$$p = p^* \exp\left[-\frac{\Delta H_{\text{vap,m}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{6.4}$$

where p^* is the vapour pressure at some temperature T^*.

Equation (6.4) can be regarded as the relationship between pressure and boiling point for a liquid as it indicates states where liquid and vapour coexist.

Example 6.2

The boiling temperature of water is 373.15 K at normal atmospheric pressure. If the enthalpy of evaporation at this temperature is 40.656 kJ mol^{-1}, calculate the pressure at which water boils at 90 °C.

From Equation (6.4), with $p^* = 1013.25\,\text{mbar}$ and $T^* = 373.15\,\text{K}$:

$$p = 1013.25 \exp\left[-\frac{40656\,\text{J mol}^{-1}}{8.314\,\text{J mol}^{-1}\,\text{K}^{-1}}\left(\frac{1}{363.15} - \frac{1}{373.15}\right)\right]\text{mbar}$$
$$\underline{= 706\,\text{mbar}}$$

Note: The tabulated value for p_s of water at 90 °C is 701.1 mbar (ref. (e), p. 150). The difference is probably because the temperature-dependence of the enthalpy of evaporation has not been taken into account in this calculation.

The evaporation of a substance at a temperature below its normal boiling point by pressure reduction has significant practical importance. It means that processes such as distillation and drying can be carried out at significantly lower temperatures than normal. This reduces the risk of thermal decomposition and means that energy sources at lower temperatures can be used.

6.2.2. Distillation

In distillation, the boiling point of, say, a binary mixture is related to its composition. The composition of the vapour can be related to that of the liquid by means of Raoult's law.

Raoult's law states that, for ideally behaving mixtures, the vapour pressure (p_1) of a particular component (1) above the liquid, depends on the mole fraction (x_1) of liquid 1 in the mixture:

$$p_1 = x_1 p_1^* \tag{6.5}$$

where p_1^* is the vapour pressure of the pure liquid at the temperature involved.

In a binary mixture of volatile liquids (component 1 + component 2) showing ideal behaviour, Equation (6.5) gives:

$$p_l = x_1 p_1^*$$

and

$$p_2 = x_2 p_2^* \tag{6.5a}$$

Since

$$\begin{aligned} p_{\text{total}} &= p_1 + p_2 \\ &= x_1 p_1^* + x_2 p_2^* \end{aligned}$$

then

$$p_{\text{total}} = p_2^* + x_1(p_1^* - p_2^*) \tag{6.6}$$

Note: In Equation (6.6), the subscript 1 normally refers to the substance of higher volatility.

Equation 6.6 shows that, at a given temperature, the total pressure depends on the composition of the liquid. The line relating p_{tot} and x_{liq} represents conditions where liquid and vapour are in equilibrium.

Raoult's law is obeyed when the components in the mixture are closely related. With dissimilar components, deviations from Equation (6.5) can be marked. If, however, small amounts of a component are present (for example, if the component in excess is thought of as the 'solvent' and the component present in small amounts as the 'solute') then at low x_{solute} values, Henry's law, Equation (6.7) is obeyed:

$$p_{\mathrm{solute}} = x_{\mathrm{solute}} K_{\mathrm{solute}} \tag{6.7}$$

where K_{solute} is the Henry's law constant for that component. K_{solute} is obtained from vapour pressure vs x_{solute} data at low x_{solute} values.

When a liquid and vapour are in equilibrium, their compositions are not necessarily the same. For example, if one component has a higher volatility than the other, the vapour will be richer in the more volatile component. If y_1 and y_2 represent the composition of the vapour phase:

$$y_1 = \frac{p_1}{p_{\mathrm{total}}}$$

and

$$y_2 = \frac{p_2}{p_{\mathrm{total}}} \tag{6.8}$$

From Equations (6.5a) and (6.6):

$$y_1 = \frac{x_1 p_1^*}{p_2^* + x_1(p_1^* - p_2^*)} \tag{6.9}$$

and

$$y_2 = 1 - y_1 \tag{6.10}$$

Equations (6.8) to (6.10) show the relationship between the vapour and liquid compositions when the two phases are in equilibrium. The dependence of the vapour composition on total pressure can be expressed as:

$$p_{\mathrm{total}} = \frac{p_1^* p_2^*}{p_1^* + (p_2^* - p_1^*) y_1} \tag{6.11}$$

Example 6.3

Ethylene glycol has a vapour pressure of 20 mbar at 100 °C. Butanol has a vapour pressure of 500 mbar at approximately the same temperature. The boiling temperatures for butanol and ethylene glycol at normal atmospheric pressure are 117.9 °C and 198 °C, respectively.

(a) What is the composition of the mixture that will boil at 100 °C when the total pressure is 400 mbar?
(b) What is the composition of the vapour produced?

(a) From Equation (6.6) with 1 = butanol:

$$p_{\text{total}} = p^*_{\text{gly}} + x_{\text{BuOH}}\,(p^*_{\text{BuOH}} - p^*_{\text{gly}})$$

$$\therefore \quad 400\,\text{mbar} = 20\,\text{mbar} + x_{\text{BuOH}}\,(500 - 20)\,\text{mbar}$$

$$\therefore \quad x_{\text{BuOH}} = \frac{380\,\text{mbar}}{480\,\text{mbar}}$$

$$= 0.792$$

$$\therefore \quad x_{\text{gly}} = (1 - x_{\text{BuOH}})$$

$$= \underline{0.208}$$

(b) From Equation (6.9):

$$y_{\text{BuOH}} = \frac{x_{\text{BuOH}}\,p^*_{\text{BuOH}}}{p^*_{\text{gly}} + x_{\text{BuOH}}(p^*_{\text{BuOH}} - p^*_{\text{gly}})}$$

$$\therefore \quad y_{\text{BuOH}} = \frac{0.792 \times 500\,\text{mbar}}{20\,\text{mbar} + (0.792 \times 480)\,\text{mbar}}$$

$$= 0.99$$

$$y_{\text{gly}} = \underline{0.01}$$

Example 6.4

A pressure-dependent separation factor α for two substances present in a binary mixture can be defined:

$$\alpha = \frac{p^*_1}{p^*_2}$$

It is a measure of the higher volatility component in the vapour and is therefore important in the separation of mixtures by distillation. As the temperature of vaporisation is lowered (equivalent to a reduction of total pressure), α increases.

(a) From Equation (6.9), derive an expression equivalent to α.
(b) At 90 °C, the vapour pressure of toluene is 532 mbar and that of *o*-xylene is 199.5 mbar. If a mixture that boils at 90 °C at 0.5 atm has a toluene mole fraction of 0.92, what is the composition of the vapour?

(a) A measure of the higher volatility component is the ratio y_1/y_2 where y_1 is given in Equation (6.9)

$$\therefore \quad \frac{y_1}{y_2} = \frac{y_1}{(1 - y_1)}$$

$$y_1 = \frac{x_1 p_1^*}{p_2^* + x_1(p_1^* - p_2^*)}$$

$$y_2 = 1 - \frac{x_1 p_1^*}{p_2^* + x_1(p_1^* - p_2^*)}$$

$$= \frac{p_2^* - x_1 p_2^*}{p_2^* + x_1(p_1^* - p_2^*)}$$

$$\therefore \quad \frac{y_1}{y_2} = \frac{x_1 p_1^*}{(1 - x_1)p_2^*} = \underline{\frac{x_1 p_1^*}{x_2 p_2^*}}$$

(b)

$$\frac{y_1}{y_2} = \frac{x_1}{x_2}\frac{p_1^*}{p_2^*}$$

$$= \frac{0.92}{0.08}\frac{532}{199.5}$$

$$\therefore \quad \frac{y_1}{(1 - y_1)} = 30.667$$

$\therefore$ $\underline{y_1 = \text{(mf toluene)} = 0.97 \text{ and } y_2 \text{ (mf } o\text{-xylene)} = 0.03}$

6.2.3 Evaporation (Drying)

The removal of, for example, water vapour by evaporation is the basis of drying operations. If a liquid–vapour equilibrium is established, the rate of evaporation and the rate of vapour condensation are equal, and the corresponding pressure at a particular temperature is the vapour pressure of the liquid at that temperature.

From Equation (1.18), the area-related condensation rate can be obtained:

$$j_{\mathrm{N,cond}} = \sigma_{\mathrm{cond}} \frac{n_{\mathrm{vap}}\bar{c}}{4} \tag{6.12}$$

where σ_{cond} is the surface condensation coefficient, n_{vap} is the vapour particle number density and $\bar{c}/4$ is the mean normal component of velocity of vapour particles (see Chapter 1).

If the vapour formed above a liquid (or a solid such as ice) is continuously removed by pumping or by a flow of vapour-free gas, the equilibrium described above cannot be established and the maximum area-related evaporation rate is obtained. This is:

$$j_{\mathrm{N,evap}} = \sigma_{\mathrm{cond}} \frac{n_{\mathrm{sat}}\bar{c}}{4} \tag{6.13}$$

where n_{sat} is the vapour particle number density if saturation was established.

From Equation (1.5):

$$n_{\mathrm{sat}} = \frac{p_{\mathrm{sat}}}{kT}$$

If the area-related mass evaporation rate is required then

$$j_{m,evap} = n_{\mathrm{sat}}\, m_{\mathrm{vap}} \frac{\sigma_{\mathrm{cond}}\bar{c}}{4}$$

where m_{vap} is the mass of the vapour particles ($= M_{\mathrm{vap}}/N_{\mathrm{A}}$).

From the above, with $\bar{c} = (RT/2\pi M)^{1/2}$ (Equation 1.14):

$$j_{\mathrm{m,evap}} = 4.38 \times 10^{-3}\, \sigma_{\mathrm{cond}}\, p_{\mathrm{sat}} \sqrt{\frac{M}{T}}\,\mathrm{kg\,s^{-1}\,m^{-2}} \tag{6.14}$$

with (p_{sat}) measured in Pa.

Note: The drying operation is more efficient if the vapour produced is removed either by sweeping it away with a dry gas or removing it with a vacuum pump.

1 If vapour molecules are not completely removed (due to insufficient pumping speed or due to the presence of the same vapour in the sweeping gas stream), the above evaporation rate will be reduced.

2 Equation (6.14) predicts the mass flow at temperature T. In many cases, evaporation leads to a reduction in temperature unless the appropriate amount of energy is available to maintain isothermal conditions.

Example 6.5

(a) Calculate the maximum area-related pV-throughput for the evaporation of water at 20 °C if a condensation coefficient, $\sigma_{\text{cond}} = 0.02$ is assumed.

(b) If water vapour at pressure p already exists above the evaporating liquid surface, how is the pV-throughput affected?

(c) If a vacuum pump is used to remove water vapour, how can the maximum throughput be maintained?

((a) based on Example 15.2, p. 567, ref. (d′) with permission)

(a) At 20 °C, water has a saturated vapour pressure of 23.4 mbar.
From Equation (6.14), the maximum area-related evaporation rate is:

$$
\begin{aligned}
j_{\text{m,evap}} &= 4.38 \times 10^{-3} \times 0.02 \times 23.4 \times 10^{2}\,\text{Pa} \times \sqrt{\frac{18}{293}}\,\text{kg}\,\text{s}^{-1}\,\text{m}^{-2} \\
&= 0.05\,\text{kg}\,\text{s}^{-1}\,\text{m}^{-2} \\
&= 50\,\text{g}\,\text{s}^{-1}\,\text{m}^{-2}
\end{aligned}
$$

From: $$q_{pV} = \dot{m} \times \frac{RT}{M}$$

$$
\begin{aligned}
q_{pV,\text{evap,max}} &= \frac{50\,\text{g}\,\text{s}^{-1}\,\text{m}^{-2} \times 83.14\,\text{mbar}\,\text{L}\,\text{mol}^{-1}\,\text{K}^{-1} \times 293\,\text{K}}{18\,\text{g}\,\text{mol}^{-1}} \\
&= \underline{6.8\,\text{mbar}\,\text{L}\,\text{s}^{-1}\,\text{cm}^{-2}}
\end{aligned}
$$

(b) If water vapour is already present above the evaporating liquid, $q_{pV,\text{evap,max}}$ will be reduced to a value:

$$q_{pV,\text{evap}} = q_{pV,\text{evap,max}}\left(1 - \frac{p}{p_{\text{sat}}}\right)$$

(c) To establish $q_{pV\text{evap,max}}$, the vacuum pump must remove all the vapour evaporating from the liquid. The required pumping speed is:

$$S_{\text{eff}} \geq \frac{q_{pV\text{evap,max}}}{p_{\text{sat}}}$$

$$\geq \frac{6.8\,\text{mbar L s}^{-1}\,\text{cm}^{-2}}{23.4\,\text{mbar}}$$

$$\geq 0.29\,\text{L s}^{-1}\,\text{cm}^{-2} \text{ of evaporating water}$$

For example, if $A_{H_2O} = 100\,\text{cm}^2$, a pump with $S_{\text{eff}} \geq 29\,\text{L s}^{-1}$ would be required for vapour removal.

Example 6.6

Moisture is to be removed, in a drier, from compacted material with a microcrystalline structure. The drier, fitted with a heating jacket and a regulator to maintain a constant temperature, is charged with 100 kg product containing 30% water. The final product must have a residual moisture of 0.1% or less. Because of the nature of the product, its temperature should not exceed 50 °C and, to achieve the required dryness, a pressure of 2 mbar is required. It is proposed to carry out the process with a single-stage oil-sealed rotary pump ($S_{\text{eff}} = 100\,\text{m}^3\,\text{h}^{-1}$, water vapour tolerance = 50 mbar at 40 °C and p_{ult} (with gas ballast) = 1 mbar).

(a) Calculate the drying time if leakage into the system is negligible.
(b) Calculate the energy requirement of the drier if the enthalpy of evaporation of water is $43.31\,\text{kJ mol}^{-1}$.
(c) If no external heating is used, estimate the effect.

(a) The water vapour tolerance of the pump is 50 mbar, this means that p_{sat,H_2O} must not exceed this value. The corresponding temperature for 50 mbar is approximately 33 °C (see tables of the variation of saturation pressure of water with temperature, for example ref. (e), p. 150).

The water vapour tolerance of a pump is the maximum pressure of pure water vapour that the pump can take in and transport. Example 3.3 indicates how this is calculated.

In this case:

$$q_{pV,H_2O,\max} = p_{H_2O,1} \times S_{\text{eff}}$$

where $p_{H_2O,1}$ is the water vapour tolerance (see Equation (3.4))

$$= 50\,\text{mbar} \times 27.8\,\text{L s}^{-1}$$

$$= 1389\,\text{mbar L s}^{-1}$$

From: $$q_{pV} = \dot{m}\frac{RT}{M}$$

$$\dot{m}_{H_2O,max} = \frac{1389\,\text{mbar L s}^{-1} \times 18\,\text{g mol}^{-1}}{83.14\,\text{mbar L mol}^{-1}\,\text{K}^{-1} \times 313\,\text{K}}$$
$$= 0.96\,\text{g s}^{-1}$$
$$= 3.46\,\text{kg h}^{-1}$$

If this is 'free' water, *i.e.* water not trapped in capillaries or dissolved in the product, then the drying time (t) will be:

$$t = \frac{29.9\,\text{kg}}{3.46\,\text{kg h}^{-1}}$$
$$\underline{= 8.6\,\text{h}}$$

In this case, the material is microcrystalline and when 'free' water has been removed, 'bound' water (in the internal structure and dissolved in the product) must be evaporated. This will evolve at a lower rate, extending the drying time. Further, the pump in this case has an ultimate pressure, with gas ballast, of 1 mbar. Because of the characteristics of such pumps (see Chapter 3), S_{eff} is not constant throughout the pressure range and will be declining below about 10 mbar. This will extend the drying time further.

In practice, with industrial drying operations, it is usual to set a required time. Using a useful rule-of-thumb (see 'Vacuum Technology for Chemical Engineering', publication no. 00.180.02, Leybold, Cologne, p. 30) to estimate $\dot{m}_{max,H_2O}$:

$$\dot{m}_{max,H_2O} = 2 \times \frac{m_{tot}}{t_{tot}}$$

S_{eff} can be calculated.

(b) At a constant rate of water removal of 3.46 kg h^{-1} and with an enthalpy of evaporation of 43.31 kJ mol^{-1} (= 2406.2 kJ kg^{-1}), the energy requirement of the heater for isothermal evaporation can be calculated:

$$\Delta Q = 9.6 \times 10^{-4}\,\text{kg s}^{-1} \times 2406.2\,\text{kJ kg}^{-1}$$
$$\underline{= 2.31\,\text{kW}}$$

(c) If this energy is not supplied to the evaporating water, a temperature fall in the product will occur.

The heat removed from the water would be 2.31 kJ s^{-1}

$$\therefore \quad -2.31\,\text{kJ s}^{-1} = m_{H_2O} \times C_{p,H_2O} \times \Delta T$$

where $C_{p,\mathrm{H_2O}}$ is the specific heat capacity of water (4.193 kJ kg^{-1} K^{-1}) and ΔT is the temperature change.

$$\therefore \quad \Delta T = \frac{-2.31\,\mathrm{kJ\,s^{-1}}}{1\,\mathrm{kg} \times 4.193\,\mathrm{kJ\,kg^{-1}\,K^{-1}}}$$
$$= -0.55\,\mathrm{K\,s^{-1}}$$

Very approximately, this would mean that after 20 s the temperature of the evaporating water would have fallen by about 11 K. The water temperature, if initially at 25 °C, would be 14 °C, thereby lowering the saturation vapour pressure of water and further extending the drying time. Continued evaporation without externally supplied energy would eventually lead to the water freezing and further prolong the process.

6.2.4 Condensers

In Example 6.6, the drying time (and the required S_{eff}) could have been greatly reduced by increasing the process temperature. A water vapour pressure would have been generated, however, which would have considerably exceeded the tolerance of the pump. By the use of an appropriate vacuum-side condenser, this could be avoided.

Condensers are heat exchangers that transfer the heat of condensation of vapour to a coolant. They are useful devices in the removal of large amounts of vapour from a gas stream. Depending on the application, it may be useful to condense the majority of the vapour generated in a vacuum process by inserting a condenser between the vessel and the pump, and use a small vacuum pump to remove non-condensable gases.

In a condenser, the rate of heat flow ($\dot{Q}$) is proportional to the condenser area (A), the mean temperature difference (ΔT_{m}) between the coolant and vapour streams and the overall coefficient of heat transfer (k):

$$\dot{Q} = A \Delta T_{\mathrm{m}} k \tag{6.15}$$

The constant k takes into account the heat flow from the warm vapour to a coolant flowing behind a metal wall (tube). Its reciprocal represents the sum of thermal resistances on the gas side, at the wall and on the coolant side.

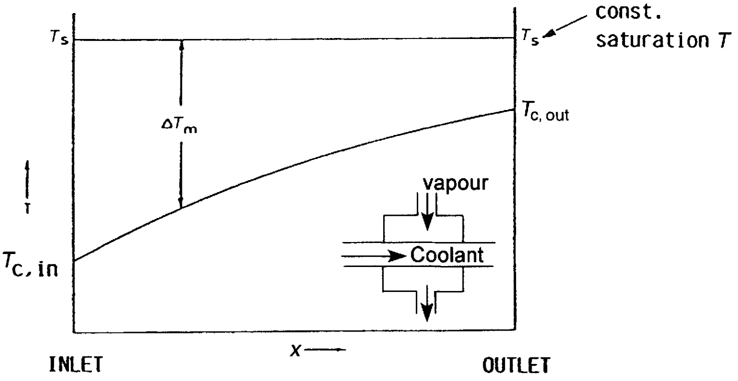
In an ideal condenser (Figure 6.1(a)) containing only vapour at a constant pressure (p_{vap}) throughout, the temperature of the coolant increases from that at the inlet ($T_{\mathrm{c,in}}$) to that at the outlet ($T_{\mathrm{c,out}}$) because of the absorbed heat flux ($\dot{Q}$). The actual temperature rise is determined by the mass flow rate of the coolant ($\dot{m}_{\mathrm{c}}$):

$$T_{\mathrm{c,out}} - T_{\mathrm{c,in}} = \frac{\dot{Q}}{c_{\mathrm{p,c}} \times \dot{m}_{\mathrm{c}}} \tag{6.16}$$

where $c_{p,\mathrm{c}}$ is the specific heat capacity of the coolant.

In practice, condenser temperatures are as shown in Figure 6.1(b) (both vapour and coolant temperatures change) and in the equation for ($\dot{Q}$), the log mean temperature difference should be used for ΔT_{m}.

(a) Ideal condenser



(b) Real condenser

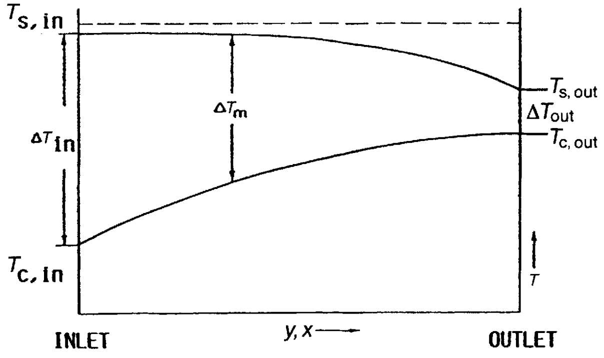


Figure 6.1 *Variation of vapour temperature (T_s) and coolant temperature (T_c) for a coil-type condenser; see ref. (g)*

$$\Delta T_m = \frac{\Delta T_{in} - \Delta T_{out}}{\ln (\Delta T_{in}/\Delta T_{out})} \tag{6.17}$$

$$\text{where} \quad \Delta T_{in} = T_{vap,in} - T_{c,in}$$

$$\Delta T_{out} = T_{vap,out} - T_{c,out}$$

(see, for example, T. D. Eastop and A. McConkey, *Applied Thermodynamics for Engineering Technologists*, 4th Edn., Longman Scientific and Technical, Harlow, 1986, p. 719).

For $\Delta T_{in}/\Delta T_{out} < 3$, an error of less than 10% is introduced if the simple mean is taken $(\Delta T_{in} = (\Delta T_{in} + \Delta T_{out})/2)$.

Example 6.7

It is decided to reduce the overall drying time in Example 6.6 to 5 h by raising the temperature to 45 °C and inserting a coiled tube condenser ($k = 1200\,\mathrm{W\,m^{-2}\,K^{-1}}$) between the drier and the pump ($S_{eff} = 100\,\mathrm{m^3\,h^{-1}}$).

(a) Calculate the amount of vapour to be removed by the condenser if it leaves the condenser at 20 °C.
(b) Estimate the required condenser surface if cooling water is used which enters the condenser at 12 °C and leaves at 16 °C. Take the enthalpy of condensation of vapour to be $40.656\,\mathrm{kJ\,mol^{-1}}$.

(a) According to Example 6.6:

$$\dot{m}_{max} = 2 \times \frac{m_{tot}}{t_{tot}}$$

$$\therefore \quad \dot{m}_{max} = 2 \times \frac{29.9\,\mathrm{kg}}{5\,\mathrm{h}}$$

$$= 11.96\,\mathrm{kg\,h^{-1}}$$

Water vapour at 20 °C has a saturated vapour pressure of 23.37 mbar. The maximum pV-throughput leaving the condenser will be given by:

$$q_{pV,H_2O,pump} = 23.37\,\mathrm{mbar} \times 27.78\,\mathrm{L\,s^{-1}}$$

$$= 649.2\,\mathrm{mbar\,L\,s^{-1}}$$

$$\therefore \quad \dot{m}_{H_2O,pump} = \frac{q_{pV} \times M}{RT}\,\mathrm{g\,s^{-1}}$$

$$= 0.48\,\mathrm{g\,s^{-1}}$$

$$= 1.73\,\mathrm{kg\,h^{-1}}$$

$\therefore$ Amount of water vapour to be removed by the condenser

$$\underline{= 10.23\,\text{kg}\,\text{h}^{-1}}$$

(b) The condensation of $10.23\,\text{kg}\,\text{h}^{-1}$ of water vapour requires:

$$\begin{aligned}\dot{Q} &= 10.23\,\text{kg}\,\text{h}^{-1} \times 2258.7\,\text{kJ}\,\text{kg}^{-1}\\ &= 6.42\,\text{kJ}\,\text{s}^{-1}\\ &= 6.42\,\text{kW}\end{aligned}$$

From Equation (6.15):

$$A = \frac{\dot{Q}}{\Delta T_\text{m} k}$$

In this case, ΔT_m is given by Equation (6.17)

$$\Delta T_\text{m} = \frac{\Delta T_\text{in} - \Delta T_\text{out}}{\ln\,(\Delta T_\text{in}/\Delta T_\text{out})}$$

$$\begin{aligned}\text{where}\quad \Delta T_\text{in} &= 45\,°\text{C} - 12\,°\text{C} = 33\,\text{K}\\ \text{and}\quad \Delta T_\text{out} &= 20\,°\text{C} - 16\,°\text{C} = 4\,\text{K}\\ \therefore\quad \Delta T_\text{m} &= 13.7\,\text{K}\\ \therefore\quad A &= \frac{6.42\,\text{kW}}{13.7\,\text{K} \times 1200\,\text{W}\,\text{m}^{-2}\,\text{K}^{-1}}\\ &\underline{= 0.4\,\text{m}^2}\end{aligned}$$

The usual situation found with condensers is that the incoming gas contains both vapour and permanent gas (usually due to air in-leakage). This means that:

$$p_\text{tot,in} = p_\text{vap,in} + p_\text{air,in}$$

In a condenser in which both condensable and non-condensable components enter, at the exit the partial pressure of the condensable has been reduced whilst that of the permanent gas fraction has increased. These pressure changes can be calculated. For example, if a gas flow consisting of vapour + air enters a condenser then:

$$q_{pV,\text{tot,in}} = q_{pV,\text{vap,in}} + q_{pV,\text{air,in}}$$

A further aspect which must be considered is that although in an ideal condenser the inlet and outlet pressures may be identical, a pressure drop (realistically 30%) occurs because of conductance losses.

Or:

$$\dot{m}_{\text{tot,in}} = \dot{m}_{\text{vap,in}} + \dot{m}_{\text{air,in}}$$

where

$$\dot{m}_x = q_{pV,x} \times \frac{M_x}{RT}$$

and

$$q_{pV,x} = p_x \dot{V}$$

where $\dot{V}$ is the volume rate of flow entering the condenser.

Further:

$$p_{\text{tot,in}} = p_{\text{vap,in}} + p_{\text{air,in}}$$

$$\therefore \quad \frac{p_{\text{vap,in}}}{p_{\text{tot,in}}} = \frac{p_{\text{vap,in}}}{p_{\text{vap,in}} + p_{\text{air,in}}}$$

and, from the expressions for $\dot{m}_x$ and $q_{pV,x}$ above:

$$\frac{p_{\text{vap,in}}}{p_{\text{tot,in}}} = \frac{\dot{m}_{\text{vap,in}}/M_{\text{vap}}}{(\dot{m}_{\text{vap,in}}/M_{\text{vap}}) + (\dot{m}_{\text{air,in}}/M_{\text{air}})} \tag{6.18}$$

A similar expression can be obtained for $p_{\text{air,in}}/p_{\text{tot,in}}$ from which:

$$\frac{p_{\text{vap,in}}}{p_{\text{air,in}}} = \frac{\dot{m}_{\text{vap,in}}/M_{\text{vap}}}{\dot{m}_{\text{air,in}}/M_{\text{air}}} \tag{6.19}$$

Example 6.8

A mixture consisting of 95% water vapour and 5% air enters a condenser in which 90% of the water is condensed.

(a) Calculate what proportion of the total pressure of gases at the inlet and outlet of the condenser is water vapour.
(b) Calculate what proportion of the original mass flow has to be dealt with by a vacuum pump fitted after the condenser.

(Based on Example 9.1, p. 320, ref. (d′) with permission)

(a)

$$\begin{aligned}\dot{m}_{\text{tot,in}} &= \dot{m}_{\text{H}_2\text{O,in}} + \dot{m}_{\text{air,in}} \\ &= 0.95\dot{m}_{\text{tot,in}} + 0.05\dot{m}_{\text{tot,in}}\end{aligned}$$

From Equation (6.18),

$$\left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{tot}}}\right)_{\text{in}} = \frac{0.95\dot{m}_{\text{tot,in}}/18}{(0.95\dot{m}_{\text{tot,in}}/18) + (0.05\dot{m}_{\text{tot,in}}/29)}$$

∴ 97% of the total pressure of incoming gases is water vapour.

$$\begin{aligned}\dot{m}_{\text{tot,out}} &= \dot{m}_{\text{H}_2\text{O,out}} + \dot{m}_{\text{air,out}} \\ &= (0.95 \times 0.1)\dot{m}_{\text{tot,in}} + 0.05\dot{m}_{\text{tot,in}} \\ &= 0.095\dot{m}_{\text{tot,in}} + 0.05\dot{m}_{\text{tot,in}} \\ \therefore \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{tot}}}\right)_{\text{out}} &= \frac{0.095\dot{m}_{\text{tot.in}}/18}{(0.095\dot{m}_{\text{tot,in}}/18) + (0.05\dot{m}_{\text{tot.in}}/29)} \\ &= \underline{0.75}\end{aligned}$$

∴ 75% of the total pressure of gases leaving the condenser is water vapour.

(b) The proportion is given by:

$$\begin{aligned}\frac{\dot{m}_{\text{tot,out}}}{\dot{m}_{\text{tot,in}}} &= \frac{(0.095 + 0.05)\dot{m}_{\text{tot,in}}}{\dot{m}_{\text{tot,in}}} \\ &= 0.145 \\ &= 14.5\%\end{aligned}$$

6.2.5 Condenser and Vacuum Pump Combinations

In vacuum processes which use inlet condensers to remove substantial amounts of vapour, the associated pumping system is used to maintain the required working pressure by removing any uncondensed vapour and permanent gas from air in-leakage, usually leaving the condenser. A typical system is shown in Figure 6.2.

In Figure 6.2, the size (S_{eff}) of the pumping system required depends on the working pressure, the gas temperature at the condenser outlet and the total leakage into the system. Further, the mass flow rate of vapour leaving the condenser which may cause emissions depends on the leak-tightness of the system. In Figure 6.2, assume that, in the outlet stream

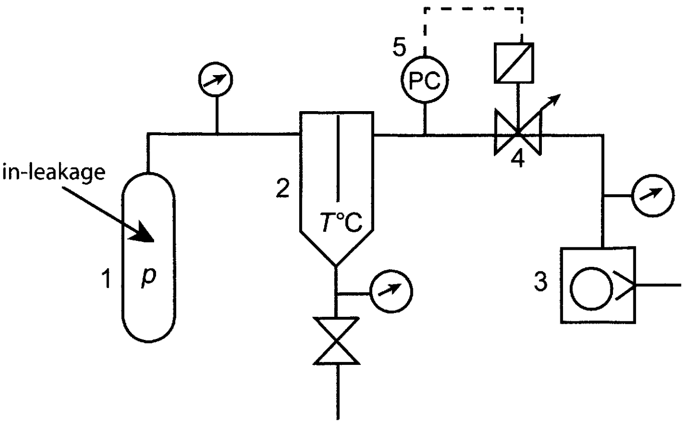


Figure 6.2 *Schematic diagram of a vacuum system with a condenser between the vacuum vessel and the pump:* (1) *vessel at working pressure* p; (2) *condenser, coolant at* T °*C;* (3) *vacuum pump (*S_{eff} at condenser outlet); (4) *throttle valve;* (5) *pressure controller*

from the condenser, there is vapour (p_{vap}) and air (p_{air}) at total pressure p_{tot}.

$$\left(\frac{p_{vap}}{p_{tot}}\right)_{out} = \frac{\dot{m}_{vap,out}/M_{vap}}{\dot{m}_{vap,out}/M_{vap} + \dot{m}_{air,out}/M_{air}} \tag{6.20}$$

$$\left(\frac{p_{air}}{p_{tot}}\right)_{out} = \frac{\dot{m}_{air,out}/M_{air}}{\dot{m}_{vap,out}/M_{vap} + \dot{m}_{air,out}/M_{air}} \tag{6.21}$$

Dividing Equation (6.20) by Equation (6.21) gives:

$$\left(\frac{p_{vap}}{p_{air}}\right)_{out} = \frac{\dot{m}_{vap,out}/M_{vap}}{\dot{m}_{air,out}/M_{air}}$$

Rearranging gives:

$$\dot{m}_{vap,out} = \dot{m}_{air,out} \times \frac{M_{vap}}{M_{air}} \times \left(\frac{p_{vap}}{p_{air}}\right)_{out} \tag{6.22}$$

From $\dot{m}_{vap,out}$ in Equation (6.22), $q_{pV,vap,out}$ can be obtained.

Similarly, $q_{pV,air,out}$ can be found from $\dot{m}_{vap,out}$ and, from the total throughput, S_{eff} can be obtained.

Example 6.9

Toluene is to be removed from a vacuum vessel working at 100 mbar in a system of the type shown in Figure 6.2 The condenser outlet system is at 10 °C, and the vapour pressure of toluene at 10 °C is 16 mbar.

(a) If air is leaking into the system at a rate of 0.5 kg h^{-1} and there is a pressure drop of 30% across the condenser, calculate S_{eff} for the vacuum pump.

(b) If air is leaking into the system at a rate of 1 kg h^{-1}, calculate the mass flow rate of toluene at the outlet of the condenser.

For the condenser:

(a)

$$\begin{aligned} \dot{m}_{\text{air,out}} &= \dot{m}_{\text{air,in}} = 0.5\,\text{kg}\,\text{h}^{-1} \\ &= 0.139\,\text{g}\,\text{s}^{-1} \end{aligned}$$

$$\begin{aligned} p_{\text{tot,out}} &= p_{\text{air,out}} + p_{\text{vap,out}} \\ p_{\text{tot,out}} &= \left(p_{\text{tot,in}} - \frac{30}{100} p_{\text{tot,in}}\right) \\ &= 100 - 30\,\text{mbar} \\ &= 70\,\text{mbar} \\ p_{\text{vap,out}} &= 16\,\text{mbar} \\ \therefore \quad p_{\text{air,out}} &= 54\,\text{mbar} \end{aligned}$$

Further:

$$q_{pV,\text{tot,out}} = q_{pV,\text{vap,out}} + q_{pV,\text{air,out}}$$

From Equation (6.22):

$$\begin{aligned} \dot{m}_{\text{vap,out}} &= \dot{m}_{\text{air}} \frac{M_{\text{vap}}}{M_{\text{air}}} \left(\frac{p_{\text{vap}}}{p_{\text{air}}}\right) \\ &= 0.138\,\text{g}\,\text{s}^{-1} \times \frac{92.13}{29} \times \left(\frac{16}{54}\right) \\ &= 0.131\,\text{g}\,\text{s}^{-1} \end{aligned}$$

From Equations (2.2) and (2.4):

$$\begin{aligned} q_{pV,\text{vap,out}} &= \frac{0.131\,\text{g}\,\text{s}^{-1}}{92.13\,\text{g}\,\text{mol}^{-1}} \times 83.14\,\text{mbar}\,\text{L}\,\text{mol}^{-1}\,\text{K}^{-1} \times 283\,\text{K} \\ &= 33.4\,\text{mbar}\,\text{L}\,\text{s}^{-1} \end{aligned}$$

Similarly:

$$q_{pV,\text{air,out}} = \frac{0.139\,\text{g s}^{-1} \times 83.14\,\text{mbar L mol}^{-1}\,\text{K}^{-1} \times 283\,\text{K}}{29\,\text{g mol}^{-1}}$$

$$= 112.8\,\text{mbar L s}^{-1}$$

$$\therefore \quad q_{pV,\text{tot,out}} = 146.2\,\text{mbar L s}^{-1}$$

$$\text{As} \quad q_{pV,\text{tot,out}} = p_{\text{tot,out}} \times S_{\text{eff}}$$

$$S_{\text{eff}} = \underline{2.09\,\text{L s}^{-1}\ (7.5\,\text{m}^3\,\text{h}^{-1})}$$

(b) From Equation (6.22):

$$\dot{m}_{\text{vap,out}} = 0.278\,\text{g s}^{-1} \times \frac{92.13}{29} \times \left(\frac{16}{54}\right)$$

$$= \underline{0.262\,\text{g s}^{-1}}\ \text{(double the mass flow in (a))}$$

If emissions from the condenser are likely to exceed the allowable limits in the atmosphere for such substances, a further pump outlet condenser may be required.

6.3 UHV SYSTEMS

Because of the extreme sensitivity of many materials and processes to residual gas, it is highly desirable to minimise or even eliminate the influence of the vacuum system in which the examination or process is being carried out. The use of UHV systems is obviously desirable and work involving such systems has allowed significant advances to be made in understanding some technologically important phenomena. Just two examples are (i) investigations using surface analysis techniques (LEED, XPS, AES, *etc.*) in UHV systems and (ii) the increasing use, in several areas of research, of light produced in synchrotron radiation sources based on electron or positron UHV storage rings.

In all vacuum systems, the pressure obtained is determined by the gas load and the effective pumping speed. In UHV systems at equilibrium, the predominant gas load arises from the outgassing of the internal surfaces. Although gas sources in vacuum systems have been discussed in Chapter 4, no differentiation was made between gas adsorbed on a surface and that absorbed within its structure. Various applications of UHV technology involve the use of vacuum systems that cannot be baked *in situ* and consideration of the choice of material for the vacuum envelope and also its surface treatment is critical. An important starting point for this is an understanding of the interaction of gas with materials.

6.3.1 Factors Influencing Outgassing

6.3.1.1 Adsorption/desorption. Gas can stick to surfaces either by physisorption or chemisorption. Generally, in physisorption, there is a weak Van der Waals interaction between the surface and the adsorbed species. The enthalpy of adsorption is about the same as the enthalpy of condensation, *e.g.* the maximum observed values of the enthalpy of physisorption of H_2, N_2 and H_2O are −84, −21 and 57 kJ mol^{-1}, respectively. (In chemisorption, the adsorbing species sticks to the surface as a result of chemical bond formation. The energies involved are much greater than in physisorption.)

A physisorbed molecule vibrates in a shallow potential well. Since the binding energy is low, it may readily break free. The rate of escape is considered to follow an Arrhenius-type law:

$$k_{\mathrm{des}} = A \exp(-E_{\mathrm{des}}/RT) \tag{6.23}$$

To desorb, the energy of the species must be $\geq E_{\mathrm{des}}$. The average residence time (τ) of the molecule on the surface can be identified as $1/k_{\mathrm{des}}$.

If $1/A = \tau_0$, then Equation (6.23) becomes:

$$\tau = \tau_0 \exp(E_{\mathrm{des}}/RT) \tag{6.24}$$

where τ_0 is the frequency of vibration of the molecule–surface bond. Weak molecule–surface bonds vibrate with a frequency (ν) of about $10^{12}\,\mathrm{s}^{-1}$ (oscillation period about 10^{-12} s); chemisorbed species have an oscillation period of about 10^{-14} s.

If there are N sites on a surface to which molecules can be attached, the rate of desorption will be proportional to the number of adsorbed species. For example, if a surface has N_0 particles attached to it initially (time $t = 0$) and, after a time t, some have desorbed, then N_t can be given as:

$$N_t = N_0 \exp(-t/\tau) \tag{6.25}$$

The time to desorb to a fraction $f = N_t/N_0$, is given by:

$$t = \tau \ln \frac{1}{f} \tag{6.26}$$

If the adsorbed particles are packed to form a single layer on the surface, the coverage can be expressed as N_{ML} where ML denotes a monomolecular layer (monolayer). If N_{ML} can be accommodated and N_t have been adsorbed, the actual number of adsorbed species is often stated in terms of the monolayer coverage so that

$$\frac{N_t}{N_{\mathrm{ML}}} = \theta$$

where θ denotes the fractional coverage of the surface in terms of the monolayer.

According to Boltzmann, if dN of N particles adsorbed have the required kinetic energy $E_{\mathrm{kin}} \geq E_{\mathrm{des}}$ ($E_{\mathrm{des}} = -E_{\mathrm{ads}}$), then they may escape. This can be stated as:

$$\mathrm{d}N = N \exp\left(-E_{\mathrm{des}}/RT\right)$$

or

$$\mathrm{d}N = N \exp\left(+E_{\mathrm{ads}}/RT\right) \tag{6.27}$$

and

$$j_{\mathrm{des}} = \frac{\mathrm{d}N}{\mathrm{d}t} = \nu_0 N \exp\left(-E_{\mathrm{des}}/RT\right) \tag{6.28}$$

where j_{des} is the desorption, flux and ν_0 is the vibrational frequency of the molecule–surface bond.

Example 6.10

(a) If the molar desorption energy of H atoms is (i) 15 kJ (ii) 150 kJ and $\tau_0 = 10^{-13}$ s, how long will an H atom remain on a surface at 298 K in cases (i) and (ii)?
(b) For case (i), what will be the residence time at 90 K?
(c) For case (ii), what will be the residence time at 1000 K?

(a) From Equation (6.24):

$$\tau = \tau_0 \exp\left(E_{\mathrm{des}}/RT\right)$$

For (i) $= 10^{-13}\,\mathrm{s} \times \exp\left[15\,000\,\mathrm{J\,mol^{-1}}/(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}} \times 298\,\mathrm{K})\right]$

$= 10^{-13}\,\mathrm{s} \times 4.26 \times 10^{2}$

$= \underline{4.3 \times 10^{-11}\,\mathrm{s}}$ (an extremely short time)

For (ii) $= 10^{-13}\,\mathrm{s} \times \exp\left[150\,000/(8.314 \times 298)\right]$

$$= 10^{-13}\,\text{s} \times 1.97 \times 10^{26}$$

$$\underline{= 1.97 \times 10^{13}\,\text{s}} \text{ (an extremely long time)}$$

(b) $$\tau = \tau_0 \exp(E_{\text{des}}/RT)$$

$$= 10^{-13}\,\text{s} \times \exp[15\,000/(8.314 \times 90)]$$

$$= 10^{-13}\,\text{s} \times 5.1 \times 10^{8}$$

$$\underline{= 5.1 \times 10^{-5}\,\text{s}}$$

(c) $$\tau = 10^{-13}\,\text{s} \times \exp[150\,000/(8.314 \times 1000)]$$

$$= 10^{-13}\,\text{s} \times 6.85 \times 10^{78}$$

$$\underline{= 6.8 \times 10^{-6}\,\text{s}}$$

Example 6.11

Laser-induced thermal desorption experiments indicate that the desorption of deuterium from a Si (111) surface has Arrhenius parameters of $10^{15.2}\,\text{s}^{-1}$ and 247 kJ mol^{-1}. Calculate the length of time required to desorb deuterium from a surface initially covered with 0.8 ML to a coverage of 0.2 ML at 720 K.

From Equation (6.26)

$$t = \tau \ln \frac{1}{f}$$

where $$f = \frac{0.2}{0.8}$$

From Equation (6.24):

$$\tau = \tau_0 \exp(E_{\text{des}}/RT)$$

If $$\tau_0 = \frac{1}{A}$$

then, with $$A = 10^{15.2}\,\text{s}^{-1}$$

$$\tau_0 = 6.3 \times 10^{-10}\,\text{s}$$

$$\therefore \quad \tau = 6.3 \times 10^{-16} \exp[247\,000/(8.314 \times 720)]\,\text{s}$$

$$= 6.3 \times 10^{-16} \times 8.32 \times 10^{17}\,\text{s}$$

$$= 524\,\text{s}$$

$$\therefore \quad t = 524\,\text{s} \times \ln \frac{0.8}{0.2}$$

$$= \underline{726\,\text{s}}$$

Example 6.12

An austenitic stainless steel surface is covered by a monolayer of N_2.

(a) Calculate the approximate number of molecules in the layer if it is assumed that the molecules are perfect spheres having a van der Waals radius of 150 pm and are hexagonally close-packed.
(b) Estimate the time required to desorb 90% of this layer by evacuation at 293 K if the molar desorption energy for N_2 is 21 kJ mol^{-1}.
(c) Recalculate using a molar desorption energy = 120 kJ.
(d) Recalculate (c) but with $T = 150\,^\circ\text{C}$.

(a) From an appropriate sketch it can be shown that the area of the base of the unit cell for hexagonally close-packed N_2 is:

$$A = 2\sqrt{3}R^2$$

where R is the van der Waals radius.

$$A = 2\sqrt{3}(1.5 \times 10^{-10}\,\text{m})^2$$
$$= 7.8 \times 10^{-20}\,\text{m}^2$$

Assuming a 1 m^2 geometric surface, the number of molecules in the monolayer is $1/(7.8 \times 10^{-20})$. The monolayer therefore contains 1.28×10^{19} molecules per m^2.

(b) If the surface is covered at $t = 0$ and only 10% remains after t, the fraction (θ) remaining is $10/100 = 0.1$.
From Equation (6.26):

$$t = \tau \ln \frac{1}{\theta}$$

and from Equation (6.24):

$$\tau = \tau_0 \exp\,(E_{\text{des}}/RT)$$

If $$\tau = 10^{-13}\,\text{s} \times \exp[21000\,\text{J mol}^{-1}/(8.314\text{J mol}^{-1}\,\text{K}^{-1} \times 293\,\text{K})]$$
$$= 10^{-13}\,\text{s} \times \exp\,(8.62)$$

$$= 5.6 \times 10^{-10}\,\text{s}$$

$$t = \tau \ln \frac{1}{\theta}$$

$$\therefore \quad t = 5.6 \times 10^{-10}\,\text{s} \times \ln\left(\frac{1}{0.1}\right)$$

$$= 5.6 \times 10^{-10}\,\text{s} \times 2.303$$

$$\underline{= 1.3 \times 10^{-9}\,\text{s}}$$

(c) If $E_{\text{des}} = 120\,\text{kJ mol}^{-1}$

$$\tau = \tau_0 \exp\,[120\,000/(8.314 \times 293)]$$

$$= 10^{-13}\,\text{s} \times \exp\,(49.26)$$

$$= 10^{-13}\,\text{s} \times 2.48 \times 10^{21}$$

$$= 2.4 \times 10^{8}\,\text{s}$$

$$\therefore \quad t = 2.4 \times 10^{8} \times 2.303$$

$$\underline{= 5.5 \times 10^{8}\,\text{s}}$$

(d) If $E_{\text{des}} = 120\,\text{kJ mol}^{-1}$ and $T = 423\,\text{K}$

$$\tau = 10^{-13}\,\text{s} \times 6.59 \times 10^{14}$$

$$\tau = 65.9\,\text{s}$$

$$\therefore \quad t = \underline{152\,\text{s}}$$

6.3.1.2 Diffusive Outgassing. Depending on the nature of the solid, it is possible for adsorbed gas particles to diffuse into the interior. Usually, however, gas absorption takes place during the manufacture of a material. For example, when metals and alloys are in the molten state they can absorb gas. The interaction commonly takes place during melting and casting, particularly in atmospheric air, and H_2, N_2, CO and CO_2 are usually involved. No matter what the mechanism of incorporation, the outward diffusion of absorbed gas can influence the behaviour of materials used in the construction of vacuum vessels and components, or the substrates processed in them. It is for this reason that some materials are outgassed at elevated temperatures before they are processed in or incorporated into the vacuum system.

To treat the diffusive outgassing process quantitatively but relatively simply, outgassing from a thin (thickness (= $2d$) small compared to length and breadth) sheet of material, *e.g.* metal, can be considered. This is shown in Figure 6.3.

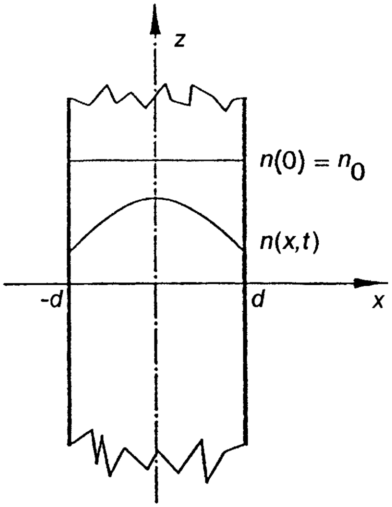


Figure 6.3 *Diffusion-controlled outgassing*

(Reproduced from ref. (d′), p. 71, with permission of F. Vieweg & Sohn Verlagsgesellschaft mbH, Wiesbaden)

At the start of the process, it is assumed that the sheet contains a uniform distribution of absorbed gas particles (number density = n_0).

The process, which involves diffusion, is initiated by a temperature rise. Under these conditions, a diffusion flux (j_{diff}) will emerge symmetrically from both sides of the sheet and the particle number density (n) will vary with time according to Fick's law:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = D\frac{\mathrm{d}^2n}{\mathrm{d}t^2}$$

where D is the diffusion coefficient, and

$$j_{\text{diff}} = -D\frac{\mathrm{d}n}{\mathrm{d}x}$$

For long outgassing times, the approximate solution to the above is:

$$j_{\text{diff}} = \frac{2D}{d} n_0 \exp\left(-\frac{\pi^2 D}{4d^2}t\right) \tag{6.29}$$

where the thickness of the sheet is $2d$ and n_0 is the initial gas content (which can be expressed in terms of the mass of absorbed particles, or the molar quantity or the number density).

The temperature-dependence of D can be expressed as:

$$D = D_0 \exp(-E_{\text{diff}}/RT) \qquad (6.30)$$

where E_{diff} is an energy term that accounts for the mechanism by which gas enters or leaves the material.

If t_a is the outgassing time constant for the process then for $t > 0.5t_a$, Equation (6.29) can be expressed as:

$$j_{\text{diff}} = j_0 \exp(-t/t_a) \qquad (6.31)$$

where

$$j_0 = \frac{2D}{d} n_0 \qquad (6.31a)$$

and

$$t_a = \frac{4d^2}{\pi^2 D} \qquad (6.31b)$$

For $t < 0.5t_a$, a further simple expression is:

$$j_{\text{diff}} = j_0 \sqrt{\frac{\pi}{16} \frac{t_a}{t}} \qquad (6.32)$$

As with desorption, an expression can also be obtained for the degree of outgassing for $f < 0.3$:

$$\frac{t}{t_a} = \ln \frac{8}{\pi^2 f} \qquad (6.33)$$

$$\text{where} \quad f = \frac{n_t}{n_0}$$

Example 6.13

The H_2 content of Inconel is 2 ppm. The density of Inconel is approximately 8000 kg m^{-3}. Express the H_2 content in terms of (a) the mass of H_2 per m^3 Inconel, (b) the molar quantity of H_2 per m^3 Inconel, (c) the particle number density.

(a) H_2 content = 2 parts H_2 in 10^6 parts Inconel.

If the density of Inconel is $8 \times 10^3 \text{kg m}^{-3}$ then the mass of H_2 per unit volume Inconel is:

$$m_{H_2} = \frac{2}{10^6} \times 8 \times 10^3 \,\text{kg m}^{-3}$$

$$\therefore \quad m_{H_2} = 16 \times 10^{-3} \,\text{kg m}^{-3}$$

$$\underline{= 1.6 \times 10^{-2} \,\text{kg m}^{-3}}$$

(b) Molar mass $H_2 = 2 \,\text{kg kmol}^{-1}$

$$\therefore \quad \text{Molar quantity of } H_2 = \frac{1.6 \times 10^{-2} \,\text{kg m}^{-3}}{M_{H_2}} = \frac{1.6 \times 10^{-2} \,\text{kg m}^{-3}}{2 \,\text{kg kmol}^{-1}}$$

$$= 8 \times 10^{-3} \,\text{kmol m}^{-3}$$

(c) $$N_A = 6.022 \times 10^{23} \,\text{mol}^{-1}$$

$$= 6.022 \times 10^{26} \,\text{kmol}^{-1}$$

$$\therefore \quad n_{H_2} = 8 \times 10^{-3} \times 6.022 \times 10^{26} \,\text{m}^{-3}$$

$$\underline{= 4.8 \times 10^{24} \,\text{m}^{-3}}$$

Example 6.14

An experimental UHV vacuum vessel used in fusion experiments is to be made of Inconel with a wall thickness of 89 mm. According to the manufacturer's data, the solubility of H_2 in Inconel is $0.4 \,\text{mbar L cm}^{-3}$ at about 1500 °C.

The vacuum requirements for the vessel demand that, at its working temperature (300 °C), no more than $3 \times 10^{-10} \,\text{mbar L s}^{-1} \text{cm}^{-2}$ H_2 should be evolved from the walls.

(a) Calculate the time required to reach this value if, for Inconel, $D_0 = 1.1 \times 10^{-6} \,\text{m}^2 \text{s}^{-1}$ and $E_{\text{diff}} = 49.9 \,\text{kJ mol}^{-1}$.

(b) If the value is too high, suggest a method by which a time to achieve an acceptable rate of diffusive outgassing could be reached and justify the method by calculation.

(a) If the solubility of H_2 in Inconel is $0.4 \,\text{mbar L cm}^{-3}$, and it is assumed that this subsequently remains in the metal then m_{H_2} can be calculated from:

$$pV = \frac{m}{M} RT$$

$$\therefore \quad m_{H_2} = \frac{pV \times M}{RT} = \frac{0.4\,\text{mbar L cm}^{-3} \times 2\,\text{g mol}^{-1}}{83.14\,\text{mbar L mol}^{-1}\,\text{K}^{-1} \times 1773\,\text{K}}$$

$$= 5.43 \times 10^{-6}\,\text{g cm}^{-3}$$

$$\underline{= 5.43 \times 10^{-3}\,\text{kg m}^{-3}}$$

From the diffusivity data and Equation (6.30):

$$D_{573\,\text{K}} = (1.1 \times 10^{-6}\,\text{m}^2\,\text{s}^{-1})\exp\left(\frac{-49900\,\text{J mol}^{-1}}{8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 573\,\text{K}}\right)$$

$$= (1.1 \times 10^{-6}\,\text{m}^2\,\text{s}^{-1}) \times (2.82 \times 10^{-}5)$$

$$= 3.11 \times 10^{-11}\,\text{m}^2\,\text{s}^{-1}$$

The initial diffusive mass flux density can be calculated from Equation (6.31a).

$$\therefore \quad j_{\text{m,diff}} = \frac{2 \times (3.11 \times 10^{-11})\,\text{m}^2\,\text{s}^{-1} \times (5.43 \times 10^{-3})\,\text{kg m}^{-3}}{(4.45 \times 10^{-2})\,\text{m}}$$

$$= 7.59 \times 10^{-12}\,\text{kg s}^{-1}\ \text{m}^{-2}$$

but, since only one side of the Inconel would outgas:

$$j_{\text{m,diff}} \underline{= 3.79 \times 10^{-12}\,\text{kg s}^{-1}\,\text{m}^{-2}}$$

$$\text{or} \quad q_{pV,\text{o,diff}} = 9 \times 10^{-9}\,\text{mbar L s}^{-1}\,\text{cm}^{-2}$$

From Equation (6.31b):

The time constant, $t_a = \dfrac{4d^2}{\pi^2 D}$

$$\underline{= 2.58 \times 10^7\,\text{s}}\ (299\ \text{days})$$

After 100 days, the amount of outgassing can be calculated from Equation (6.32).

$$\therefore \quad j_{100,\text{diff}} = j_{0,\text{diff}}\sqrt{\frac{\pi}{16}\frac{t_a}{t}}$$

$$j_{100,\text{diff}} = 9 \times 10^{-9}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \times 0.77$$

$$\underline{= 6.9 \times 10^{-9}\,\text{mbar L s}^{-1}\,\text{cm}^{-2}}$$

This value indicates that diffusive outgassing would be too high even after 3 months of use.

(b) In such cases, it is usual to degas the chamber at higher temperatures. Inconel can be baked to a maximum of 550 °C before unacceptable changes to its mechanical properties would occur. This should be carried out.

At 550 °C (823K):

$$D_{823\text{K}} = 1.1 \times 10^{-6}\,\text{m}^2\,\text{s}^{-1} \times \exp(-6002\,\text{K}/823\,\text{K})$$

$$= \underline{7.49 \times 10^{-10}\,\text{m}^2\,\text{s}^{-1}}$$

$$\therefore \quad j_{\text{m,diff}} = \frac{2D}{d} \times \text{mass content of } \text{H}_2$$

$$= \frac{2 \times 7.49 \times 10^{-10}\,\text{m}^2\,\text{s}^{-1} \times 5.43 \times 10^{-3}\,\text{kg}\,\text{m}^{-3}}{4.45 \times 10^{-2}\,\text{m}}$$

$$= 1.83 \times 10^{-10}\,\text{kg}\,\text{s}^{-1}\,\text{m}^{-2}$$

For one side only:

$$j_{\text{m,diff}} = 9.2 \times 10^{-11}\,\text{kg}\,\text{s}^{-1}\,\text{m}^{-2}\ (3.15 \times 10^{-7}\,\text{mbar L s}^{-1}\,\text{cm}^{-2})$$

$$t_a = \frac{4d^2}{\pi^2 D}$$

$$= 4 \times \frac{(4.45 \times 10^{-2})^2}{\pi^2 \times 7.49 \times 10^{-10}}$$

$$= 1.1 \times 10^6\,\text{s (12 days)}$$

For $t > 0.5t_a$, Equations (6.31) applies

$$\therefore \quad 3 \times 10^{-10}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} = 3.15 \times 10^{-7}\,\text{mbar L s}^{-1}\,\text{cm}^{-2} \exp(-t/t_a)$$

$$\therefore \quad 9.53 \times 10^{-4} = \exp(-t/t_a)$$

$$\therefore \quad \ln(9.53 \times 10^{-4}) = \frac{-t}{t_a}$$

$$\therefore \quad -7 = \frac{-t}{12\text{ days}}$$

$$\therefore \quad t = \underline{84\text{ days}}$$

This is a considerable improvement on (a).

Example 6.15

A cylindrical UHV chamber ($d = 50\,\text{cm}$, $h = 60\,\text{cm}$) is to be constructed from an air-melted austenitic stainless steel (thickness = 5 mm). Apart from surface cleaning, no other treatment will be carried out. It is proposed to use the chamber for LEED/RHEED studies at 300 K and a pressure of 5×10^{-10} mbar. It will be pumped with an appropriate pump having $S_{\text{eff},H_2} = 1000\,\text{L}\,\text{s}^{-1}$ in the HV/UHV range. If gas sources other than diffusive outgassing can be ignored, calculate the pressure that can be achieved after 2 weeks pumping. Take D_0 and E_{diff} for stainless steel = $12 \times 10^{-6}\,\text{m}^2\,\text{s}^{-1}$ and $54\,800\,\text{J}\,\text{mol}^{-1}$, respectively; assume air-melted stainless steel contains 6 ppm H_2 and its density is $7900\,\text{kg}\,\text{m}^{-3}$.

From Equation (6.30) and the given diffusivity data:

$$
\begin{aligned}
D_{300\,\text{K}} &= 1.2 \times 10^{-6}\,\text{m}^2\,\text{s}^{-1} \exp(-6591\,\text{K}/300\,\text{K}) \\
&= 1.2 \times 10^{-6}\,\text{m}^2\,\text{s}^{-1} \times 2.87 \times 10^{-10}\,\text{m}^2\,\text{s}^{-1} \\
&= \underline{3.45 \times 10^{-16}\,\text{m}^2\,\text{s}^{-1}}
\end{aligned}
$$

H_2 content of the steel (6 ppm)

$$
\begin{aligned}
&= \frac{6}{10^6} \times 7900\,\text{kg}\,\text{m}^{-3} \\
&= 4.74 \times 10^{-2}\,\text{kg}\,\text{m}^{-3} \\
j_{\text{m},H_2O} &= \frac{2D}{d} \times \text{mass content of } H_2 \\
&= \frac{2 \times 3.45 \times 10^{-16}\,\text{m}^2\,\text{s}^{-1} \times 4.74 \times 10^{-2}\,\text{kg}\,\text{m}^{-3}}{2.5 \times 10^{-3}\,\text{m}} \\
&= 1.31 \times 10^{-14}\,\text{kg}\,\text{s}^{-1}\,\text{m}^{-2}
\end{aligned}
$$

However, since only one side of the metal is involved

$$
\begin{aligned}
&= \underline{0.66 \times 10^{-14}\,\text{kg}\,\text{s}^{-1}\,\text{m}^{-2}} \\
t_a &= \frac{4d^2}{\pi^2 D} = \frac{4 \times (2.5 \times 10^{-3})^2\,\text{m}^2}{\pi^2 \times 3.45 \times 10^{-16}\,\text{m}^2\,\text{s}^{-1}} \\
&= \frac{2.5 \times 10^{-5}\,\text{m}^2}{3.41 \times 10^{-15}} \\
&= \underline{7.3 \times 10^9\,\text{s}}\ (84\,978\ \text{days})
\end{aligned}
$$

For $t < t_a$, Equation (6.32) must be used:

$$j_{\mathrm{diff}} = j_{\mathrm{m,H_2O}}\sqrt{\frac{\pi}{16}\frac{t_a}{t}}\,\mathrm{kg\,s^{-1}\,m^{-2}}$$

For $t = 14$ days:

$$\begin{aligned} j_{\mathrm{diff}} &= j_{\mathrm{m,H_2O}}\sqrt{\frac{\pi}{16}\frac{8.5\times10^4}{14}} \\ &= j_{\mathrm{m,H_2O}} \times 34.52\,\mathrm{kg\,s^{-1}\,m^{-2}} \\ &= 2.28\times10^{-13}\,\mathrm{kg\,s^{-1}\,m^{-2}} \end{aligned}$$

For $A = 1.34\,\mathrm{m^2}$:

$$\begin{aligned} j_{diff} &= 3.05\times10^{-13}\,\mathrm{kg\,s^{-1}} \\ &= 3.05\times10^{-10}\,\mathrm{g\,s^{-1}} \\ \therefore\quad q_{pV} &= \underline{3.80\times10^{-6}\,\mathrm{mbar\,L\,s^{-1}}} \\ \therefore\quad p_{base} &= \underline{3.80\times10^{-9}\,\mathrm{mbar}} \end{aligned}$$

Required pressure would not be achieved. A degassing of the chamber at higher temperatures would be required.

6.4 SYSTEMS INVOLVING DIFFERENTIAL PUMPING

Differential pumping is a technique which is widely applied when an interface must be established between systems in which very large pressure differences exist. An excellent example is the coupling of mass spectrometers (normal working pressure 10^{-5} mbar or below) to higher pressure systems such as GC columns (in GC-MS; GC columns at 1 bar) or flow tubes (at a few mbar) in kinetics studies or molecular beam sampling.

Example 6.16

Two chambers are separated by a thin wall in which there is an orifice ($d = 0.1$ mm). If the pressure in one chamber is maintained at 10^3 mbar with N_2 at 293 K and the second chamber is evacuated with a turbomolecular pump having $S_{\mathrm{eff}} = 150\,\mathrm{L\,s^{-1}}$, what pressure will be established in the pumped chamber?

From Equation (1.44) it can be shown that when the pressure downstream of the orifice is reduced to the critical pressure and below, the mass flow through the orifice achieves a steady value:

$$q_{\mathrm{m}} = A_{\mathrm{or}}\, p_0 \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\gamma-1}} \left(\frac{2\gamma}{\gamma+1} \cdot \frac{M}{RT_1}\right)^{1/2}$$

where, in this case p_0 and T_0 are the gas pressure and temperature, respectively, in the first chamber, A_{or} is the area of the orifice, $\gamma = C_p/C_V$ (for $N_2 = 1.4$).

For $d = 0.1\,\mathrm{mm}\ (1 \times 10^{-4}\,\mathrm{m})$, $R = 8314\,\mathrm{Pa\,m^3\,kmol^{-1}\,K^{-1}}$, $\mathrm{p_0} = 10^5\,\mathrm{Pa}$,

$$q_{pV} = 7.85 \times 10^{-9}\,\mathrm{m^2} \times 10^5\,\mathrm{Pa} \times \left(\frac{2}{2.4}\right)^{2.5} \sqrt{\frac{2.8}{2.4} \times \frac{8314\,\mathrm{Pa\,m^3\,kmol^{-1}} \times 293\,\mathrm{K}}{28\,\mathrm{kg\,kmol^{-1}}}}$$

$$= 5 \times 10^{-4}\,\mathrm{Pa\,m^2} \times 318.59\,\mathrm{Pa^{1/2}\,m^{3/2}\,kg^{-1/2}}$$

$$= 0.16\,\mathrm{Pa\,m^3\,s^{-1}}$$

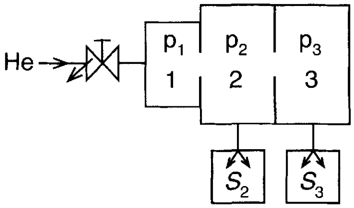
$$= 1.6\,\mathrm{mbar\,L\,s^{-1}}$$

$$\therefore \quad p_{\mathrm{ch.2}} = \frac{1.6\,\mathrm{mbar\,L\,s^{-1}}}{150\,\mathrm{L\,s^{-1}}}$$

$$\underline{= 1.1 \times 10^{-2}\,\mathrm{mbar}}$$

Example 6.17

A proposed He cluster source is shown below:



He gas is admitted to chamber 1 and maintained at a pressure p_1 = 1 mbar. At one end of chamber 1 there is an orifice ($d = 5\,\mathrm{mm}$). Chamber 2 is pumped and its pressure should ideally be $5 \times 10^{-2}\,\mathrm{mbar}$. At the end of chamber 2 there is a further orifice ($d = 5\,\mathrm{mm}$) leading to chamber 3. Chamber 3 is pumped by a $3000\,\mathrm{L\,s^{-1}}$ pump and should be maintained at a pressure $\leq 10^{-4}\,\mathrm{mbar}$. Calculate $S_{\mathrm{eff,2}}$ and p_3 if $T = 293\,\mathrm{K}$.

From Table 1.2: $\bar{l}p_{\mathrm{He,293\,K}} = 19 \times 10^{-3}\,\mathrm{cm\,mbar}$

$$\therefore \quad \text{At} \quad 1\,\mathrm{mbar},\ \bar{l}_{\mathrm{He}} = 1.9 \times 10^{-2}\,\mathrm{cm}$$

$$\therefore \quad Kn = \frac{\bar{l}}{d_{\mathrm{or,1}}} = \frac{1.9 \times 10^{-2}}{0.5} = 3.8 \times 10^{-2}$$

For $Kn < 0.01$, viscous flow is established. If it is assumed that viscous flow predominates in this case then, from Section 1.7, it can be shown that if p_2 is less than a critical value (p^*), then choked flow will occur through the orifice and the maximum value for the throughput (q_{m}^*) under choked flow conditions can be calculated.

From Equation (1.39), p^* can be calculated:

$$p^* = p_1\left(\frac{2}{\gamma + 1}\right)^{\gamma/\gamma - 1}$$

In this case, $p_1 = 1\,\mathrm{mbar}\ (100\,\mathrm{Pa})$ and $\gamma = 1.63$

$$\therefore \quad \underline{p^* = 0.49\,\mathrm{mbar}}$$

In Example 1.24, the expression for q_{m}^* was given:

$$q_{\mathrm{m}}^* = A_{\mathrm{or}}\,p_0\left(\frac{2}{\gamma + 1}\right)^{1/\gamma - 1}\left(\frac{2\gamma}{\gamma + 1}\,\frac{M}{RT_0}\right)^{1/2}$$

In this case, $A_{\mathrm{or}} = 1.96 \times 10^{-5}\,\mathrm{m}^2$, $p_0 = p_1 = 100\,\mathrm{Pa}$, $M = 4\,\mathrm{kg\,kmol}^{-1}$, $T_0 = 293\,\mathrm{K}$ and $R = 8314\,\mathrm{Pa\,m}^3\,\mathrm{kmol}^{-1}\,\mathrm{K}^{-1}$.

$$q_{\mathrm{m}}^* = 1.96 \times 10^{-5}\,\mathrm{m}^2 \times 100\,\mathrm{Pa} \times \left(\frac{2}{2.63}\right)^{1/0.63}\left(\frac{3.26 \times 4\,\mathrm{kg\,kmol}^{-1}}{2.63 \times 8314\,\mathrm{Pa\,m}^3\,\mathrm{kmol}^{-1}\,\mathrm{K}^{-1} \times 293\,\mathrm{K}}\right)^{1/2}$$

$$= 1.81 \times 10^{-6}\,\mathrm{kg\,s}^{-1}$$

$$\therefore \quad \underline{q_{pV} = 11\,\mathrm{mbar\,L\,s}^{-1}}\ \text{(chamber 1 to chamber 2)}$$

In chamber 2, gas will leave through the orifice to chamber 3 and will also be removed by pump S_2.

At $p = 5 \times 10^{-2}$ mbar and $d = 5$ mm for the orifice to chamber 3, it can be shown that $Kn = 0.76$. This corresponds to molecular flow.

The gas flow from chamber 2 to chamber 3 can be calculated from Equation (2.6) where $\Delta p = p_2 - p_3$. $C_{\mathrm{or},2\rightarrow3}$ can be calculated from Equation (2.22).

For He at 293 K:

$$\bar{c} = 1245\ \mathrm{m\,s^{-1}}$$

$$\therefore \quad C_{\mathrm{or,He}} = 31.1\ \mathrm{L\,s^{-1}\,cm^{-2}}$$

$$\begin{aligned}\therefore \quad C_{\mathrm{or},2\rightarrow3} &= 31.1\ \mathrm{L\,s^{-1}\,cm^{-2}} \times A_{\mathrm{or},2\rightarrow3} \\ &= 31.1\ \mathrm{L\,s^{-1}\,cm^{-2}} \times 0.196\ \mathrm{cm^{-2}} \\ &= 6.1\ \mathrm{L\,s^{-1}}\end{aligned}$$

$$\begin{aligned}\therefore \quad q_{pV,2\rightarrow3} &= 6.1\ \mathrm{L\,s^{-1}}(\Delta p) \\ &= 6.1\ \mathrm{L\,s^{-1}} \times 5 \times 10^{-2}\ \mathrm{mbar}\ (p_3 \text{ can be ignored}) \\ &= \underline{0.31\ \mathrm{mbar\,L\,s^{-1}}}\end{aligned}$$

From a steady-state flux balance of flow entering and leaving chamber 2:

$$q^*_{pV} = q_{pV,2\rightarrow3} + q_{pV,\mathrm{S}_2}$$

$$\therefore \quad 11\ \mathrm{mbar\,L\,s^{-1}} = 0.31\ \mathrm{mbar\,L\,s^{-1}} + 5 \times 10^{-2}\ \mathrm{mbar} \times S_{\mathrm{eff},2}$$

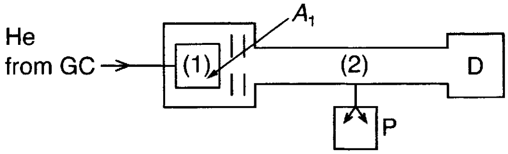
$$\therefore \quad S_{\mathrm{eff},2} = \underline{214\ \mathrm{L\,s^{-1}}}$$

If: $S_{\mathrm{eff},3} = 3000\ \mathrm{L\,s^{-1}}$ and $q_{pV,2\rightarrow3} = 0.31\ \mathrm{mbar\,L\,s^{-1}}$

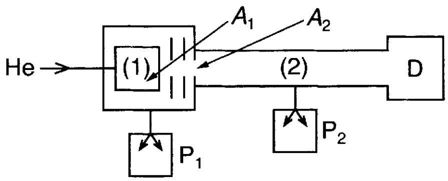
$$\begin{aligned}p_3 &= \frac{0.31}{3000}\ \mathrm{mbar} \\ &= \underline{1 \times 10^{-4}\ \mathrm{mbar}}\ \text{(as required)}\end{aligned}$$

Example 6.18

GC-MS (gas chromatography-mass spectrometry) is widely used in the analysis of complex mixtures of organic compounds. Such a system is operating with a carrier gas (He) flow through the column of 20 atm cc min^{-1} at 293 K. Since the pressure requirements of the GC and the MS differ by several orders of magnitude, two possible systems are considered (see diagrams (a) and (b)).



(1) = ion source
(2) = analyser with attached detector (D)
A_1 = represents the area of the ion source exit ports (= 0.08 cm^2)
P = pump (S_{eff} = 50 L s^{-1}, independent of gas type)



In (b), an additional restriction (A_2) has been inserted so that only 10% of the gas flow entering (1) passes to (2). Further, both the ion source area and the analyser are separately pumped ($S_{\text{eff},P_1} = S_{\text{eff},P_2} = 50\ \text{L s}^{-1}$).

If a pressure of 10^{-2} to 10^{-3} mbar is acceptable in the ion source but a pressure of $\leq 3 \times 10^{-5}$ mbar is required in the analyser (for ion transmission and detector operation), evaluate systems (a) and (b) and comment on the potential analytical sensitivity of the system.

System (a)

To establish $p_2 = 3 \times 10^{-5}$ mbar with $S_{\text{eff}} = 50\ \text{L s}^{-1}$:

$$\begin{aligned} q_{pV} \text{ for the ion source} \rightarrow \text{analyser} &= p_2 S_{\text{eff}} \\ &= 1.5 \times 10^{-3}\ \text{mbar L s}^{-1} \\ &(= 0.09\ \text{atm cc min}^{-1}) \end{aligned}$$

The pressure established in (1) given this gas throughput can be estimated from the conductance of A_1. If the ion source temperature is 200 °C then, assuming molecular flow, the conductance ($C_{A_1,\text{He}}$) at 200 °C can be calculated from Equation (2.22). For He at 200 °C, $\bar{c} = 1582\ \text{m s}^{-1}$ ($\bar{c}/4 = 396\ \text{m s}^{-1}$)

$$\begin{aligned} \therefore \quad C_{A_1,\text{He},200\,°\text{C}} &= 39.6\ \text{L s}^{-1}\ \text{cm}^{-2} \times A_1 \\ &= 39.6\ \text{L s}^{-1}\ \text{cm}^{-2} \times 0.08\ \text{cm}^{-2} \\ &= 3.2\ \text{L s}^{-1} \end{aligned}$$

$$\therefore \quad p_1 = \frac{1.5 \times 10^{-3}\,\text{mbar L s}^{-1}}{3.2\,\text{L s}^{-1}}$$

(The conductance of A_1 will throttle S_{eff,p_1} to approximately this value)

$$\underline{= 4.7 \times 10^{-4}\,\text{mbar}}$$

p_1 is well within the requirements. However, only $\frac{0.09}{20}$ (0.45%) of the effluent from the column is being utilised, leading to a loss in sensitivity for the analysis.

System (b)

If A_2 allows only 10% of the gas flow entering (1) to pass, then, for $p_2 = 3 \times 10^{-5}$ mbar, the flow into (1) is $10 \times 1.5 \times 10^{-3}$ mbar l s^{-1}

$$= 1.5 \times 10^{-2}\,\text{mbar L s}^{-1}\ (0.9\,\text{atm cc min}^{-1})$$

$$\therefore \quad p_1 = \frac{1.5 \times 10^{-2}\,\text{mbar L s}^{-1}}{3.2\,\text{L s}^{-1}}$$

$$\underline{= 4.7 \times 10^{-3}\,\text{mbar}}\ \text{(within the requirements)}$$

From the continuity relationship, the pressure in the vicinity of the ion optics is given by:

$$\frac{1.5 \times 10^{-2}\,\text{mbar L s}^{-1} - 1.5 \times 10^{-3}\,\text{mbar L s}^{-1}}{S_{\text{eff,P}_1}}$$

$$= \frac{0.0135\,\text{mbar L s}^{-1}}{50\,\text{L s}^{-1}}$$

$$\underline{= 2.7 \times 10^{-4}\,\text{mbar}}$$

Importantly, 10 times more column effluent can enter the ion source in system (b) than in system (a).

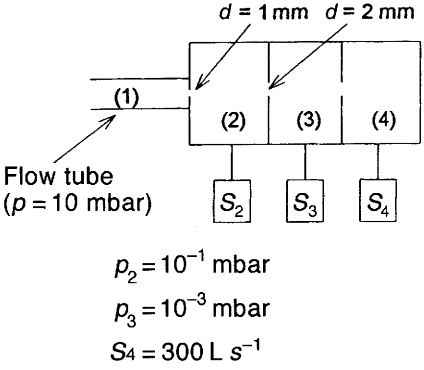
Note: Although $S_{\text{eff,P}_1} = S_{\text{eff,P}_2}$ at the point of connection, the conductance of A_1 has been calculated for He. Since C_{A_1} is gas-type-dependent under conditions of molecular flow:

$$\frac{C_{A_1,\text{He}}}{C_x} = \sqrt{\frac{M_x}{M_{\text{He}}}} \left(= \frac{S_{\text{eff,He},A_1}}{S_{\text{eff},x,A_1}} \right)$$

where x are the higher molecular weight components separated by the column. This means that S_{eff} at A_1 will vary with gas type and there will be component enrichment at A_1 and A_2.

Example 6.19

A flow-tube apparatus is connected to a photoelectron spectrometer (see diagram). The species is to be ionised in chamber 4 and a beam density of > $10^{11}\,\mathrm{cm}^{-3}$ is required. Chamber 4 is pumped with a turbomolecular pump ($S_{\mathrm{eff}} = 300\,\mathrm{L\,s^{-1}}$, independent of gas type). If He at 293 K is the carrier gas in the flow tube and the pressures and dimensions are as stated in the diagram, estimate $S_{\mathrm{eff},2}$ and $S_{\mathrm{eff},3}$.



At the 1 mm diameter orifice connecting the flow tube to chamber 2, the flow must be defined:

From Table 1.2:

$$\bar{l}p_{\mathrm{He}} = 19 \times 10^{-3}\,\mathrm{cm\,mbar\ at\ 293\,K}$$

$$\therefore \text{ At } \quad p = 10\,\mathrm{mbar},$$

$$\bar{l}_{\mathrm{He}} = 1.9 \times 10^{-3}\,\mathrm{cm}$$

$$\therefore \quad Kn = \frac{\bar{l}}{d} = \frac{1.9 \times 10^{-3}\,\mathrm{cm}}{0.1\,\mathrm{cm}} = 1.9 \times 10^{-2}$$

This value is close to that for viscous flow given in Table 1.4. Consequently, supersonic continuum flow will occur through the orifice. As the pressure in chamber 2 is below the critical pressure (4.9 mbar, see Example 6.17), a maximum gas throughput will result:

$$q_{\mathrm{m}}^* = A_{\mathrm{or}}\, p_1 \left(\frac{2}{\gamma + 1}\right)^{\frac{1}{\gamma-1}} \left(\frac{2\gamma}{\gamma + 1}\,\frac{M}{RT}\right)^{1/2}$$

In this case:

$$q_m^* = 7.85 \times 10^{-7}\,\mathrm{m}^2 \times 10^3\,\mathrm{Pa} \times 0.647 \times \left(\frac{3.26 \times 4\,\mathrm{kg\,kmol^{-1}}}{2.63 \times 8314\,\mathrm{Pa\,m^3\,kmol^{-1}\,K^{-1}} \times 293\,\mathrm{K}}\right)^{1/2}$$

$$= 7.24 \times 10^{-7}\,\mathrm{kg\,s^{-1}}$$

$$= 7.24 \times 10^{-4}\,\mathrm{g\,s^{-1}}$$

$$\therefore \quad q_{pV,\mathrm{He}} = \underline{4.41\,\mathrm{mbar\,L\,s^{-1}}}$$

For the orifice between chamber (2) and (3):

$$\bar{l}_{\mathrm{He}} = 0.19\,\mathrm{cm}$$

$$\therefore \quad \frac{\bar{l}}{d} = 0.95 \text{ (close to 1)}$$

It is assumed that molecular flow will occur through the orifice. From Example 6.17, the conductance of this orifice is:

$$C_{\mathrm{or,He}} = 31.1\,\mathrm{L\,s^{-1}\,cm^{-2}}$$

$$A_{\mathrm{or},2\to3} = 0.0314\,\mathrm{cm}^2$$

$$\therefore \quad C_{\mathrm{or},2\to3} = 0.98\,\mathrm{L\,s^{-1}}$$

$$\therefore \quad q_{pV,2\to3} = C_{\mathrm{or},2\to3} \times \Delta p_{2\to3}$$

$$= 0.98\,\mathrm{L\,s^{-1}} \times 10^{-1}\,\mathrm{mbar} \text{ (ignore } p_3 \text{ in comparison)}$$

$$= 0.098\,\mathrm{mbar\,L\,s^{-1}}$$

From the above, the throughput of gas to S_2 is:

$$q_{pV,S_2} = (4.41 - 0.098)\,\mathrm{mbar\,L\,s^{-1}}$$

$$= 4.31\,\mathrm{mbar\,L\,s^{-1}}$$

$$\therefore \quad \text{For } p_2 = 10^{-1}\,\mathrm{mbar}$$

$$\underline{S_2 = 43.1\,\mathrm{L\,s^{-1}}\ (155\,\mathrm{m^3\,h^{-1}})}$$

In chamber 4, a beam density ≥ $10^{11}\,\mathrm{cm}^{-3}$ is required. The pressure to which this corresponds is obtained from Equation (1.5):

$$p = nkT$$

$$\therefore \quad p \geq 10^{17}\,\mathrm{m}^{-3} \times 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 293\,\mathrm{K}$$

$$\geq 4 \times 10^{-4}\,\text{Pa}$$

$$\geq 4 \times 10^{-6}\,\text{mbar}$$

For $p_4 \geq 4 \times 10^{-6}\,\text{mbar}$ and $S_4 = 300\,\text{L s}^{-1}$:

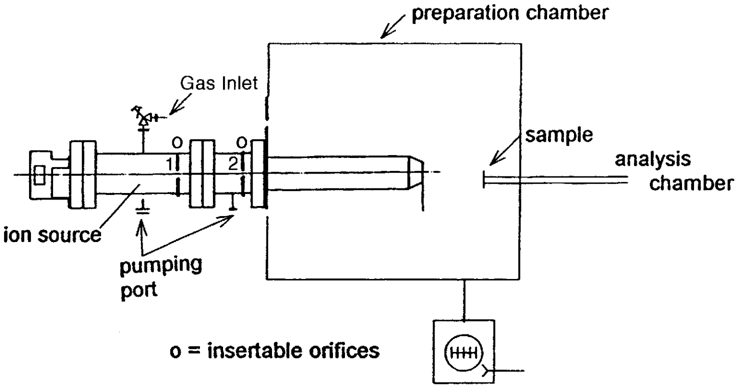
$$q_{pV,3\to4} \geq 1.2 \times 10^{-3}\,\text{mbar L s}^{-1}$$

As $q_{pV,2\to3} = 0.098\,\text{mbar L s}^{-1}$, for $q_{pV,3\to4} = 1.2 \times 10^{-3}\,\text{mbar L s}^{-1}$,
then $q_{pV,S_3} = (0.098 - 1.2 \times 10^{-3})\,\text{mbar L s}^{-1}$
$= 0.0968\,\text{mbar L s}^{-1}$
$\therefore$ To maintain $p_3 = 10^{-3}\,\text{mbar}$
$\underline{S_3 = 96.8\,\text{L s}^{-1}}$

Example 6.20

The sample preparation chamber on a surface analysis system (AES, XPS) is fitted with an ion gun for depth profiling (see diagram). The gun can be differentially pumped to maintain the required pressure difference between the ion source and the preparation chamber, which is initially fitted with a TMP with $S_{\text{eff}} = 50\,\text{L s}^{-1}$.

The sample is to be bombarded with argon ions at a minimum beam current of 1 μA with the preparation chamber at 10^{-8} mbar. The gun is operating at a current density of $1\,\text{mA cm}^{-2}$ and an electron current of 10 mA. The constant for the gun in $5\,\text{mbar}^{-1}$.



(a) For an ion current of 10 μA, calculate the Ar pressure at which the source should operate.

(b) Initially, to maintain the pressure difference between the ion source and the chamber, an orifice is inserted at position 1. Calculate the required diameter to achieve this when the preparation chamber is pumped with $S_{\mathrm{eff}} = 50\,\mathrm{L\,s^{-1}}$. (Assume the ion source temperature is 200 °C). Is the beam current requirement met?

(c) If, instead of the $50\,\mathrm{L\,s^{-1}}$ pump, one with $S_{\mathrm{eff}} = 100\,\mathrm{L\,s^{-1}}$ was used on the chamber, would the beam current requirement be met?

(d) If two identical orifices are placed in positions 1 and 2 and a pump with $S_{\mathrm{eff}} = 100\,\mathrm{L\,s^{-1}}$ is fitted on the gun chamber between the orifices, calculate the beam current if the preparation chamber is in its original configuration.

(a) $$I^- = 10\,\mathrm{mA}, \quad I^+ = 1\times10^{-5}\,\mathrm{A}, \quad K = 5\,\mathrm{mbar^{-1}}$$

From Equation (5.11):

$$I^+ = I^- K p$$

$$\therefore \quad p = \frac{\mathrm{I}^+}{I^- K}$$

$$\therefore \quad p = \frac{1\times10^{-5}\,\mathrm{A}}{1\times10^{-2}\,\mathrm{A}\times5\,\mathrm{mbar^{-1}}} = 2\times10^{-4}\,\mathrm{mbar}$$

(b) Under conditions of molecular flow at 200 °C, Ar will effuse through the orifice with an area-related volume rate of flow given in Equation (1.17).

For Ar at 200 °C, $$\bar{c} = 145.5\sqrt{\frac{T}{M}}\,\mathrm{m\,s^{-1}}$$

$$= 500.3\,\mathrm{m\,s^{-1}}$$

$$\therefore \quad \frac{\bar{c}}{4} = 125.1\,\mathrm{m\,s^{-1}}$$

$$\therefore \quad C_{\mathrm{or,Ar}} = 12.5\,\mathrm{L\,s^{-1}\,cm^{-2}}$$

To maintain 10^{-8} mbar in the preparation chamber pumped with a $50\,\mathrm{L\,s^{-1}}$ TMP:

$$q_{\mathrm{or}} = 10^{-8}\,\mathrm{mbar}\times50\,\mathrm{L\,s^{-1}}$$

$$= 5\times10^{-7}\,\mathrm{mbar\,L\,s^{-1}}$$

$$= C_{\mathrm{or,Ar}}\times A_{\mathrm{or}}\times(p_{\mathrm{source}} - p_{\mathrm{ch}})$$

$$= 12.5\,\mathrm{L\,s^{-1}\,cm^{-2}}\times A_{\mathrm{or}}\,\mathrm{cm^2}\times2\times10^{-4}\,\mathrm{mbar}\ (p_{\mathrm{ch}}\text{ is negligible})$$

$$\therefore \quad A_{\text{or}} = \frac{5 \times 10^{-7}\,\text{mbar L s}^{-1}}{12.5\,\text{L s}^{-1}\,\text{cm}^{-2} \times 2 \times 10^{-4}\,\text{mbar}}$$

$$= 2 \times 10^{-4}\,\text{cm}^2$$

$$\therefore \quad \underline{r_{\text{or}} = 8 \times 10^{-3}\,\text{cm}\ (80\,\mu\text{m})}$$

$$\text{Beam current} = 1\,\text{mA cm}^{-2} \times 2 \times 10^{-4}\,\text{cm}^2$$

$$\underline{= 2 \times 10^{-7}\,\text{A}}\ \text{(too small)}$$

(c) With the attachment of a larger pump, a larger diameter orifice is tolerable.

$$q_{\text{or}} = 10^{-8}\,\text{mbar} \times 100\,\text{L s}^{-1}$$

$$= 10^{-6}\,\text{mbar L s}^{-1}$$

$$= C_{\text{or,Ar}} \times A_{\text{or}} \times (2 \times 10^{-4})\,\text{mbar L s}^{-1}$$

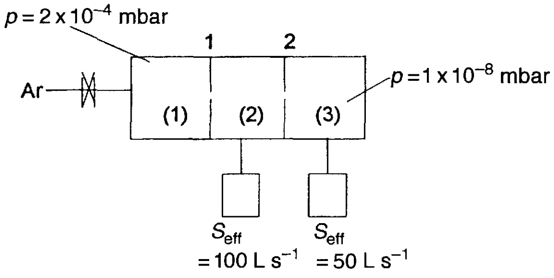
$$\therefore \quad A_{\text{or}} = \frac{10^{-6}\,\text{mbar L s}^{-1}}{12.5\,\text{L s}^{-1}\,\text{cm}^{-2} \times 2 \times 10^{-4}\,\text{mbar L s}^{-1}}$$

$$= 4 \times 10^{-4}\,\text{cm}^2$$

$$\therefore \quad \text{Beam current} = 1\,\text{mA cm}^{-2} \times 4 \times 10^{-4}\,\text{cm}^2$$

$$\underline{= 4 \times 10^{-7}\,\text{A}}\ \text{(too small)}$$

(d) With two identical orifices inserted at 1 and 2:



For chamber (1) → (2)

$$C_{\text{or}} p_{\text{source}} = p_2 \times 100\,\text{L s}^{-1} + C_{\text{or}}(p_2 - p_3)$$

$$\text{As} \quad C_{\text{or}} \ll 100\,\text{L s}^{-1} \quad \text{and} \quad p_2, p_3 \ll p_{\text{source}}$$

$$C_{\text{or}} p_{\text{source}} \cong p_2 \times 100\,\text{L s}^{-1} \quad \text{(A)}$$

For chamber (2) → (3):

$$C_{\text{or}} p_2 = p_3 \times 50\ \text{L s}^{-1} \quad \text{(B)}$$

(A) × (B):

$$C_{\text{or}}^2\, p_{\text{source}}\, p_2 = p_2 p_3 \times 100\ \text{L s}^{-1} \times 50\ \text{L s}^{-1}$$

$$\therefore \quad C_{\text{or}}^2\, p_{\text{source}} = p_3\ 100\ \text{L s}^{-1} \times 50\ \text{L s}^{-1}$$

$$\therefore \quad C_{\text{or}}^2 = \frac{p_3 \times 100\ \text{L s}^{-1} \times 50\ \text{L s}^{-1}}{2 \times 10^{-4}\ \text{mbar}}$$

$$= \frac{1 \times 10^{-8}\ \text{mbar} \times 5000\ \text{L}^2\,\text{s}^{-2}}{2 \times 10^{-4}\ \text{mbar}}$$

$$= 2.5 \times 10^{-1}\ \text{L}^2\,\text{s}^{-2}$$

$$\therefore \quad C_{\text{or}} = 0.5\ \text{L s}^{-1}$$

$$= 12.5\ \text{L s}^{-1}\,\text{cm}^{-2} \times A_{\text{or}}\ \text{cm}^2$$

$$\therefore \quad A_{\text{or}} = 0.04\ \text{cm}^2$$

$$\therefore \quad \text{Beam current} = 1\ \text{mA cm}^{-2} \times 0.04\ \text{cm}^2$$

$$= \underline{4 \times 10^{-5}}\ \text{A (acceptable)}$$

CHAPTER 7

Summary

In Chapter 1, the assumption that gases and gas mixtures behave ideally at low pressures (1 bar and below) was stated. (Deviation from this with large amounts of readily condensable vapours under compression near atmospheric pressure was dealt with in Chapter 3.) The ideal gas equation, expressing the relationship between the variables pressure, volume, temperature and amount (number of moles) of gas, together with the expression of pressure in terms of particle number density (n) and Dalton's law of partial pressures, allow many calculations useful to vacuum technology to be carried out (Examples 1.1–1.5).

The kinetic theory of gases was briefly discussed. It enables the mean or thermal velocity ($\bar{c}$) of gas molecules at a given temperature to be obtained and gas flux to be calculated. From the latter, effusion rates, area-related condensation rates and conductances under molecular flow can be determined (see Examples 1.5 and 1.7–1.10). Calculation of collision frequency (obtained from $\bar{c}$, n and the collision cross-section of molecules), enables the mean free path ($\bar{l}$) of particles to be determined. The easily obtained expression for $\bar{l}p$ is a convenient way of stating the variation of $\bar{l}$ with p (Examples 1.11–1.15).

From values of $\bar{l}$ and $\bar{c}$, the diffusion coefficient (D) and dynamic viscosity (η) can be calculated (Examples 1.16–1.19). Estimation of the Knudsen ($\bar{l}/d$) and Reynold's numbers defines the nature of gas flow (viscous, molecular, intermediate) in vacuum systems (Examples 1.20–1.22).

The chapter concluded with a section on gas dynamics (Examples 1.23–1.25).

In Chapter 2, essential terms in vacuum technology (*e.g.* *pV*-throughput, pumping speed, conductance, *etc.*) were defined. These are required for the quantification of gas loads in vacuum systems. Calculations based on relevant relationships were demonstrated (Examples 2.1–2.4).

The numerical value of the conductance of a component in a vacuum system depends on the type of flow in the system. Gas flow in simple, model systems (e.g. tubes of constant circular cross-section, orifices, apertures) was considered for viscous flow (Examples 2.6–2.8) and molecular flow (Examples 2.9–2.11). The chapter concluded with two illustrations (Examples 2.13, 2.14) of Knudsen (intermediate) flow through a tube.

Chapter 3 summarised initially the various types of vacuum pump available and the pressure ranges in which they normally operate. Subsequent sections dealt specifically with types of pump and, in some cases, to support calculations, reviewed the operating principles and characteristics. For example, aspects of oil-sealed rotary pump operation were discussed (Examples 3.1–3.5) and Roots pumps, widely used in applications where large gas loads at pressures in the rough–medium range have to be handled, were examined (Examples 3.7–3.9).

Gas-transfer pumps such as turbomolecular and diffusion pumps are extensively employed in the HV/UHV range. Both types require backing (forevacuum) pumps with the appropriate characteristics to enable their efficient performance. Aspects of the operation of diffusion pumps (Examples 3.10–3.15) and turbomolecular pumps (Examples 3.16–3.19) were considered.

Combinations of turbomolecular pumps with cryosurfaces and cryopumps are increasingly being used on 'clean' systems. Cryogenic temperatures can be achieved with liquid cryogens (see Examples 3.20, 3.21, 3.23) or commercially available two-stage cryogenerators. With non-standard cryogenic equipment, knowledge of the heat loads that may be encountered is essential. In Examples 3.22–3.24, some heat load assessments were described. Cryopump characteristics (*e.g.* pumping speed, ultimate pressure, starting pressure) are obviously important. These were examined (Examples 3.24, 3.25).

Chapter 3 also considered those entrapment pumps that remove gas particles by sorption effects such as gettering and implantation. The operating principles of sputter ion pumps were explained (Example 3.26) and some typical calculations performed (Examples 3.27–3.29). Aspects of the use of titanium sublimation pumps were dealt with (Examples 3.30–3.33).

The pressure achievable in a vacuum system depends on the effective speed of the pumps and the total gas load in the system. In Chapter 4, the usual sources of gas (leaks, outgassing, permeation) were reviewed. At the outset, terms associated with gas leakage were discussed. It can be described by the equations of flow described in Chapter 2 and quantified as a mass flow rate (and the equivalent pV-throughput and molar flow rate) (see Examples 4.1, 4.2, 4.4 and 4.8).

A typical indication of leakage is the inability of the leaking system to achieve the expected working pressure. Pressure-rise tests are frequently carried out to assess the magnitude of the problem (Examples 4.3, 4.5–4.7, 4.9). A convenient and highly sensitive method of leak detection and quantification uses He as a tracer gas and a He leak detector (MSLD). Some aspects of practical leak detection using MSLD were discussed (Examples 4.10–4.12).

Outgassing, but that due predominantly to gas adsorbed on the surface rather than incorporated within the structure, was discussed in Chapter 4. (Diffusive outgassing was discussed in Chapter 6.) Surface desorption can be described by a simple relationship containing adjustable parameters which fit measurements. The use of this formula in typical calculations was shown (Examples 4.13–4.18, 4.24).

The permeation of a gas through a substrate was described and assessment of the gas load due to permeation explained (Examples 4.19–4.23).

The concluding part of the chapter considered the influence of various gas sources on the attainable pressure in vacuum systems (Examples 4.24–4.26).

The measurement of total pressure in a vacuum system is essential. Chapter 5 outlined the two general principles involved (direct and indirect). Direct methods included manometric measurements (Examples 5.1 and 5.3) and those involving the mechanical deformation of a sensing element. Indirect methods, which depend on the estimation of a physical property of the gas (*e.g.* thermal conductivity, ionisation) that depends on number density, were also discussed. Uncertainty of measurement is a parameter associated with the result of a measurement. It may influence the choice of a pressure gauge, and its practical expression was illustrated in Example 5.4.

In connection with indirect methods, details were given of thermal conductivity vacuum gauges (*e.g.* Pirani gauges in Examples 5.5 and 5.6) and ionisation gauges. Of the latter, the two types in common use – the hot cathode and cold cathode – were described and the basic gauge equations stated. Typical calculations were given in Examples 5.7 and 5.8 (hot cathode) and Example 5.14 (cold cathode). The response of instruments involving indirect methods is dependent on gas composition. Interpretation of the indicated pressure to yield the 'true' pressure was considered in Examples 5.6, 5.9, 5.10, 5.12 and 5.13. Other gauge-specific factors were discussed including the X-ray effect for hot cathode gauges (Example 5.11) and the surprisingly high pumping effect of cold cathode gauges (Example 5.15).

Residual gas analysis with quadrupole mass spectrometers is being used increasingly in many applications for characterisation and problem diagnosis. Typical data were shown (Examples 5.16 and 5.17) and the manipulation of such data to yield partial pressures performed in Examples 5.18 and 5.19.

Chapter 6 dealt with the application of vacuum technology in three areas of the chemical sciences. The first was concerned with its use in chemical technology, particularly in purification/separation operations such as distillation and evaporation. For distillation, the use of the Clapeyron and Clausius–Clapeyron equations was demonstrated (Examples 6.1 and 6.2) whilst Raoult's and Henry's laws were stated and applied (Examples 6.3, 6.4). The removal of water (drying) is an important but poorly understood operation. Aspects of this were discussed in Examples 6.5–6.7. Condensers, particularly in conjunction with vacuum pumps, are indispensable in applications such as distillation and drying. Simple treatment of condenser theory was stated and applied in Examples 6.7–6.9.

The second application concerned aspects of UHV technology. In UHV systems at equilibrium, the predominant gas load arises from the outgassing of internal surfaces. The factors influencing outgassing, including adsorption/desorption, were discussed (Examples 6.10–6.12). Outgassing from the interior of materials (diffusive outgassing), which can arise with both metallic- and non-metallic materials exposed to vacuum, was quantified in Examples 6.13–6.15.

The third topic dealt with the widely applied technique of differential pumping which is used to create and exploit regions with large pressure differences within a system. Preliminary calculations (Examples 6.16, 6.17) indicated the procedures and typical assessments. Specific applications were given, such as GC-MS (Example 6.18), the generation and identification of unstable species (Example 6.19) and a typical ion source (used for depth profiling) (Example 6.20).

This book has presented information, in the form of worked calculations, on the background to and the current state of vacuum technology. There is no doubt that the role of vacuum technology will be equally important in the future – vacuum processing is a very effective and efficient way of handling and manufacturing materials. What will change, however, are the demands made on vacuum techniques. 'Clean' vacuum systems will be demanded which do not influence in any way the process being performed, and proof of cleanliness will be routinely confirmed in the form of high-sensitivity residual gas analysis. The need for cleanliness will also change the types of pump used. Pumps that neither influence nor are influenced by the vacuum process will be demanded. Gradually, oil-sealed pumps will be displaced by 'dry' pumps and cryosurfaces combined with turbomolecular pumps, or cryopumps, will completely replace diffusion pumps on HV/UHV systems.

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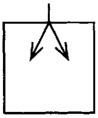
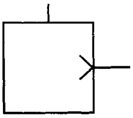
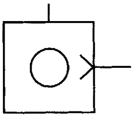
Appendix: Symbols used in Vacuum Technology according to BS 5543:1978/ISO 3753:1977



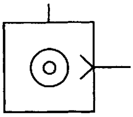
vacuum pump (type not specified)



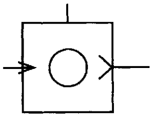
position displacement



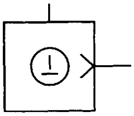
RVP (rotary vane pump)



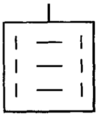
RPP (rotary piston pump)



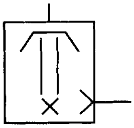
gas ballast pump



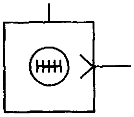
Roots pump



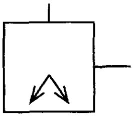
SIP



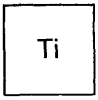
vapour diffusion pump



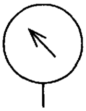
TMP



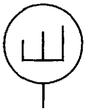
entrapment pump



TSP



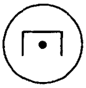
pressure gauge (type unspecified)



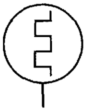
partial pressure

hot cathode ionisation gauge

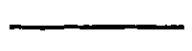
hot cathode gauge (uhv)



cold cathode ionisation gauge

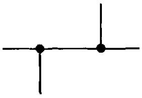


thermal conductivity gauge

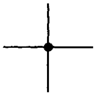


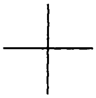
pipeline

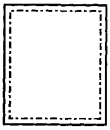
junction

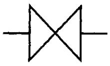


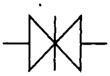
lines with junctions

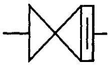

lines with cross-junction

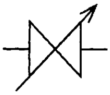

crossing lines (not connected)

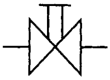

bakeable enclosure

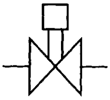

valve (type unspecified)

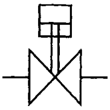

gate valve


baffle valve


fine control valve


manually operated valve


remote control valve


pneumatically-operated valve

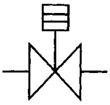

electromagnetically-operated valve

Table 1 *Nominal widths (DN) and recommended internal diameters for international standard tubes and flanges used in vacuum technology*

DN	d_i *(mm)*
10	10
16	16
25	24
40	41
63	70
100	102
125	127
160	153
250	261
630	651
1000	1000

Index

An accessible and applicable guide to quantitative problem solving in vacuum technology, this book is aimed at newcomers, students and the experienced practitioner. It contains essential information and worked examples for those using vacuum technology in chemical applications and who are involved in the design and operation of vacuum equipment.

Using step by step solutions of example calculations and formulae, ***Vacuum Technology: Calculations in Chemistry*** sets out to encourage readers to quantify their own systems so that they can ensure efficient operation and fault finding. Whilst emphasising the use of appropriate units in calculations and using well known expressions in vacuum technology throughout, the book includes:

- formulae necessary for quantitative vacuum technology
- commonly required data for common gases in tabulated form
- schematic diagrams of systems and layouts

This book is certain to be a confidence inspiring publication for use in both research and industry.

Dr David Hucknall *joined Leybold Vacuum UK Ltd in 1986 and has unrivalled expertise in vacuum technology. Since 1991 he has represented the UK on the European Working Group responsible for drafting standards on leak detection.* ***Dr Alan Morris****, currently at the University of Southampton, has over 25 years experience in the field of gas phase UV photoelectron spectroscopy. He has contributed to the design and development ofspectrometers for the study of unstable species using a wide range of radiation sources.*

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